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Hydrocarbon Emissions Reduction from Ethylene Dichloride Processes

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EPA-600/2-76-053
March 1976

HYDROCARBON EMISSIONS REDUCTION FROM ETHYLENE DICHLORIDE PROCESSES

by

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ABSTRACT

This work covers the initial phase of the development of a low-emissions ethylene oxyhydrochlorination process for producing 1,2 dichloroethane (ethylene dichloride).

Firstly, experimental work on an existing pilot plant scale, once-through process was used to obtain baseline emission data in mass of hydrocarbon plus ethylene dichloride per mass of HCl fed as a function of reactor temperature and percent excess ethylene to the reactor; and to resolve potential problems which may arise in a recycle operation, viz., whether CO is oxidized to CO_2 by the reactor, whether post-chlorination might be necessary in order to save ethylene value in the reactor exit if a CO oxidation unit were necessary, and whether the reactor would oxidize methane and ethane, thereby preventing their buildup in the recycle system.

Secondly, the existing once-through pilot plant was converted to a recycle operation which then functioned successfully and yielded emission data in mass of hydrocarbon plus ethylene dichloride per mass of HCl fed as a function of reactor temperature and percent excess ethylene to the reactor. In particular, the project objective of reducing by 90% the HC + EDC emissions from an ethylene oxyhydrochlorination process, through the recycling of reactor off-gases, has been positively demonstrated.

Thirdly, various operating difficulties were assessed which would be important for future control applications and scale-up efforts, viz., the increased sensitivity of the process to upsets in flows, temperatures, and concentrations.

Lastly, economic analyses are presented to demonstrate the competitive position of the improved process.

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16. ABSTRACT The report gives results of the initial phase of the development of a low-emissions ethylene oxyhydrochlorination process for producing 1,2-dichloroethane (ethylene dichloride). First, experimental work on an existing pilot-plant-scale, once-through process was used both to obtain baseline emission data in mass of hydrocarbon (HC) plus ethylene dichloride (EDC) per mass of HCl fed as a function of reactor temperature and percent excess ethylene to the reactor, and to resolve potential problems which may arise in a recycle operation. Second, the existing once-through pilot plant was converted to a recycle operation which then functioned successfully and yielded emission data in mass of HC plus EDC per mass of HCl fed as a function of reactor temperature and percent excess ethylene to the reactor. In particular, the project objective of reducing by 90% the HC plus EDC emissions from an ethylene oxyhydrochlorination process, through the recycling of reactor off-gases, was positively demonstrated. Third, various operating difficulties were assessed which would be important for future control applications and scale-up efforts. Economic analyses are presented to demonstrate the competitive position of the improved process.

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SECTION I

CONCLUSIONS

The conclusions appropriate for this report will be listed in the following order: (1) preliminary economic evaluation of alternative approaches; (2) experimental results for once-through operation; (3) experimental results for recycle operation; (4) emissions reduction — recycle compared to once-through; (5) simulation work (program) for scale-up; and (6) commercial plant economical study.

The preliminary economic evaluation of alternative approaches compared the proposed recycle system with catalytic oxidation and incineration. It was found that the recycle system would be considerably more economic than the other two possibilities.

The experimental results of once-through operation were:

(a) Crude ethylene dichloride (EDC) purity* varied inversely linearly with reactor temperature.

(b) Kilograms of hydrocarbon plus ethylene dichloride per kilograms of HCl emissions could be correlated as a linear function of excess ethylene to the reactor with reactor temperature as parameter.

(c) Ethylene efficiency decreases with higher operating temperature due to increased oxidation of ethylene.

(d) Addition of carbon monoxide to the feed gases indicated that CO was oxidized to CO_2; also large additions of CO_2 to the feed gases did not adversely affect the reaction.

(e) Methane passed through the reactor system unchanged and ethane was significantly reduced (80% in this case) over inlet values.

(f) Post-chlorination of excess ethylene in the reactor exit gases was feasible provided chlorine was injected into the gas phase and not the catalyst itself.

* See Glossary for definition of abbreviations.

The experimental results of recycle operation were:

(a) Crude ethylene dichloride (EDC) purity varied inversely linearly with reactor temperature, but was a few tenths of a percentage point lower than the once-through purity at the same temperature.

(b) The ethylene efficiency for the recycle operation was higher than that for the once-through process due to the recycling of off-gases.

(c) Ethylene efficiency decreases with higher operating temperature due to increased oxidation of ethylene.

(d) All runs of this report involved the recycling of greater than 90% of the reactor off-gases.

(e) Kilograms of hydrocarbon plus ethylene dichloride per kilograms of HCl emissions could be correlated as a linear function of excess ethylene to the reactor with reactor temperature as parameter.

(f) The recycle operation is more sensitive than the once-through operation and requires closer control for successful operation.

Comparison of the emissions data for once-through and recycle operation indicates that the percent reduction of HC + EDC emissions have exceeded 90% for all runs conducted in this work.

It was possible to develop a computer simulation program, based on actual experimental data, which could duplicate vent gas compositions and superficial velocities at given reactor temperatures and pressures for given excess C_2H_4/oxygen values to the reactor. The utility of this program was in its use for scale-up calculations which were used in the Incremental Economic Analysis for a commercial unit of 700 MM lbs EDC/year capacity. Based upon the optimum experimental conditions from recycle operation, viz., 230°C, 5-7% excess ethylene and 50% excess oxygen, together with this simulation program, it was found that the recycle process was competitive with existing processes to within a tenth of a percent of total incremental capital and manufacturing costs.

Finally, it is concluded that closer control of the recycle process via computer technology will overcome the inherent sensitivity of the process and lead to more consistent data and operation.

SECTION II

RECOMMENDATIONS

The work of this report has revealed that the newly-developed recycle process is much more sensitive to upsets than the conventional once-through process. This sensitivity results in an apparent narrow range of operability and difficulty in maintaining stable conditions. Before a commercial prototype of the proposed process can be designed, these sensitivity factors must be more fully explored along with the establishment of well-defined requirements necessary for stable operation. Thus, it is recommended that further work be performed on the newly-developed recycle process through the use of computer control technology to clearly delineate operating parameters affecting stability and to define the operating range of such parameters yielding satisfactory process performance.

Secondly, it is recommended that the effect of operating parameters on the existence and build-up of organic by-products (which must be vented) be investigated. Specifically, this recommendation is directed to the possible build-up of vinyl chloride in the recycle system with its consequent venting to the atmosphere.

Lastly, it is recommended that long-term, closely-controlled runs be made to determine the above mentioned build-ups of organics and also, to determine the effect of recycle operation on catalyst performance and life.

SECTION III

INTRODUCTION

GENERAL

The production of vinyl chloride in the United States is almost exclusively based on ethylene and involves three main steps:

Direct Chlorination of Ethylene —

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

Oxyhydrochlorination of Ethylene —

$$C_2H_4 + 2\ HCl + 1/2\ O_2 \longrightarrow C_2H_4Cl_2 + H_2O$$

Cracking of Ethylene Dichloride —

$$2\ C_2H_4Cl_2 \longrightarrow 2\ C_2H_3Cl + 2\ HCl$$

The overall reaction in this balanced process is —

$$2\ C_2H_4 + Cl_2 + 1/2\ O_2 \longrightarrow 2\ C_2H_3Cl + H_2O.$$

The oxyhydrochlorination step is the most technically difficult part of the overall process and has had a profound impact on the industry since its development. The first commercial ethylene oxyhydrochlorination process appeared in 1964 and within the next few years nearly 90% of the classical process for vinyl chloride from acetylene was displaced.

EXISTING PROCESS

There are currently two basic variants of ethylene oxyhydrochlorination processes, those employing fixed catalytic beds and those employing fluid catalytic beds. Most of the major producers employ a fluid bed. Ethylene, hydrogen chloride and air are introduced into the bottom of the fluid bed where the oxyhydrochlorination reaction takes place. The heat released by the reaction is substantial, so the reactors are equipped with internal cooling coils which are submerged in the fluid bed.

Downstream product recovery involves cooling of the reactor exit gases by either direct quench or a heat exchanger, followed by condensation of the ethylene dichloride product and water by-product which are separated by decantation. The remaining gases still contain 1 to 5% by volume of ethylene dichloride, so they are further processed in a secondary recovery system employing either solvent absorption or a refrigerated condenser. The off-gas is then vented to the atmosphere. See Figure 1.

The vent stream contains 85 to 95% nitrogen from the air employed as a source of oxygen for the oxyhydrochlorination reaction. It also includes a variety of other compounds which originate either in the feeds to the reactor or as by-products of the oxyhydrochlorination:

— Carbon dioxide and carbon monoxide formed by oxidation of ethylene

— Ethyl chloride formed from a side-reaction of ethylene with hydrogen chloride

— Methane and ethane which are impurities in the ethylene feed and pass through the reactor unaffected

— Ethylene dichloride which escapes from the secondary recovery system

— Solvent which escapes from the secondary recovery system

— Ethylene which is unreacted.

The aspect of most current ethylene oxyhydrochlorination processes which contributes the most to hydrocarbon emissions is the use of air as the source of oxygen. The inerts (nitrogen) accompanying the air necessitate a once-through process. If pure oxygen were used it would be possible, at least in theory, to recycle the reactor off-gases. Only one plant currently employs pure oxygen, but it does not recycle the reactor off-gases.

PROPOSED PROCESS

Recycle of reactor off-gases will eliminate the need for a secondary recovery system and the resultant losses of solvent which typically amount to 0.001 ton per

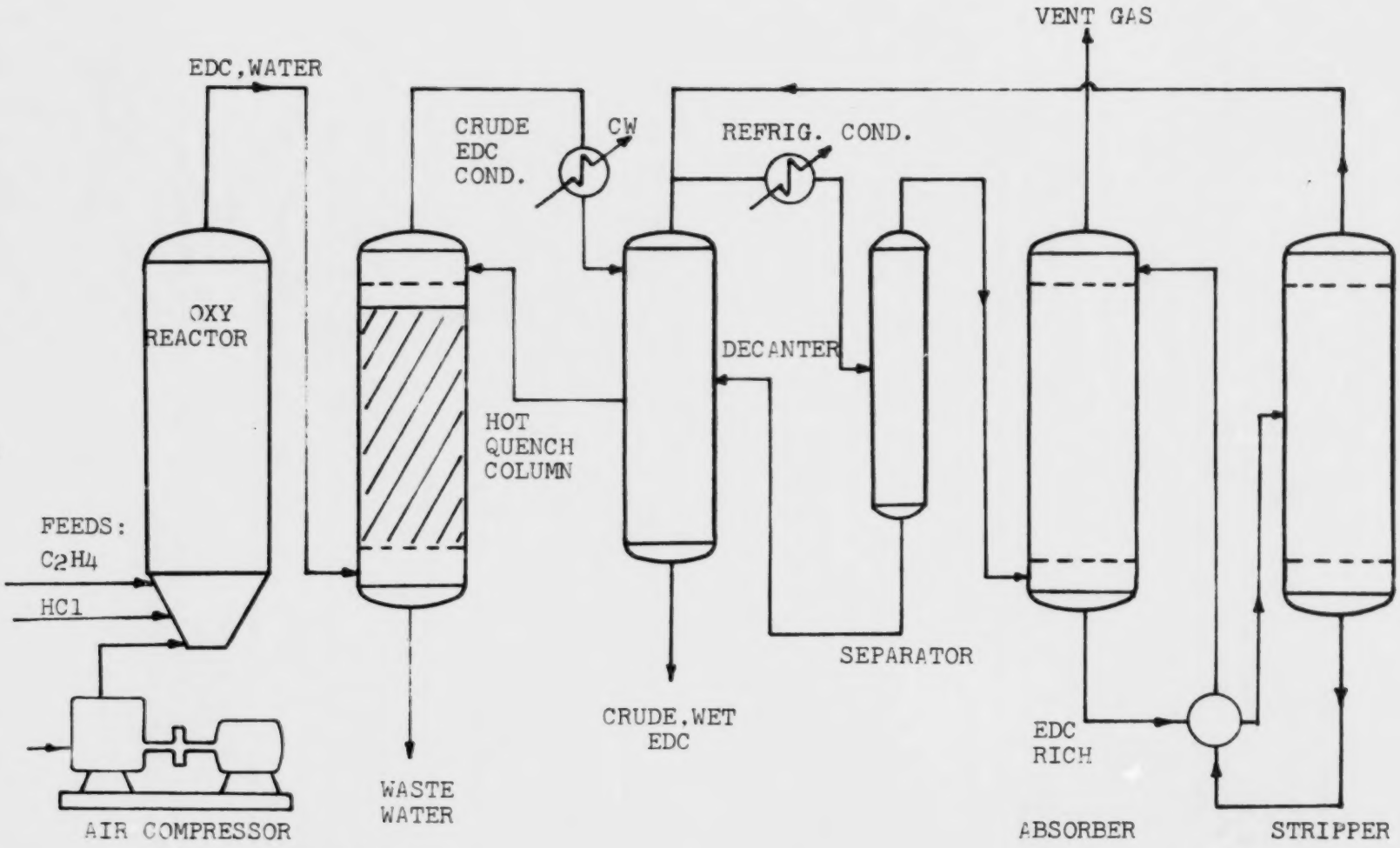


FIGURE 1:
FLOWSHEET FOR EXISTING ETHYLENE OXYHYDROCHLORINATION PROCESS

ton of EDC. It will also eliminate unreacted ethylene. Some means will have to be employed to limit build-up of feed impurities (methane and ethane) and by-products (carbon dioxide, carbon monoxide and ethyl chloride), probably a combination of removal by chemical or physical processing and a purge to atmosphere. The purge, however, will amount to only a small fraction of the vent stream which characterizes present processes and it is certainly reasonable to expect a 90% reduction in hydrocarbon emissions over present processes.

The detailed technical approach currently visualized may best be explained by reference to Figure 2 — Flowsheet for Proposed Low-Emissions Process for Producing Ethylene Dichloride by Ethylene Oxyhydrochlorination.

A fluid bed oxyhydrochlorination reactor employing a conventional copper chloride on alumina catalyst is fed with ethylene, hydrogen chloride and recycle gas containing added oxygen. The ethylene is in 5% excess over that required by the reaction stoichiometry, the oxygen in 60 to 80% excess. Near the top of the fluid bed a small stream of chlorine, amounting to 2 to 5% of the hydrogen chloride feed, is added to convert the unreacted ethylene to additional ethylene dichloride.

The gases leaving this reactor contain the products of reaction, ethylene dichloride and water, and other substances originating as unreactive impurities in the feeds or as by-products. The gases pass to a quench column where they are cooled by circulating water then to a condenser where ethylene dichloride and water are recovered. These are separated in a decanter and the non-condensable gases flow through a recuperative heat exchanger where they are re-heated.

The hot gases pass to a fixed bed oxidation reactor (shown dashed) employing a platinum on alumina catalyst where the carbon monoxide will be converted to carbon dioxide by reaction with the excess oxygen from the oxyhydrochlorination reactor. The gases exiting the reactor are cooled against the entering gases in the recuperative heat exchanger and passed to a booster compressor. It may be possible to eliminate the separate carbon monoxide oxidation step if it can be shown that CO can be oxidized to CO_2 by recycle to the oxyhydrochlorinator. If this is possible, then the need for post-chlorination is obviated.

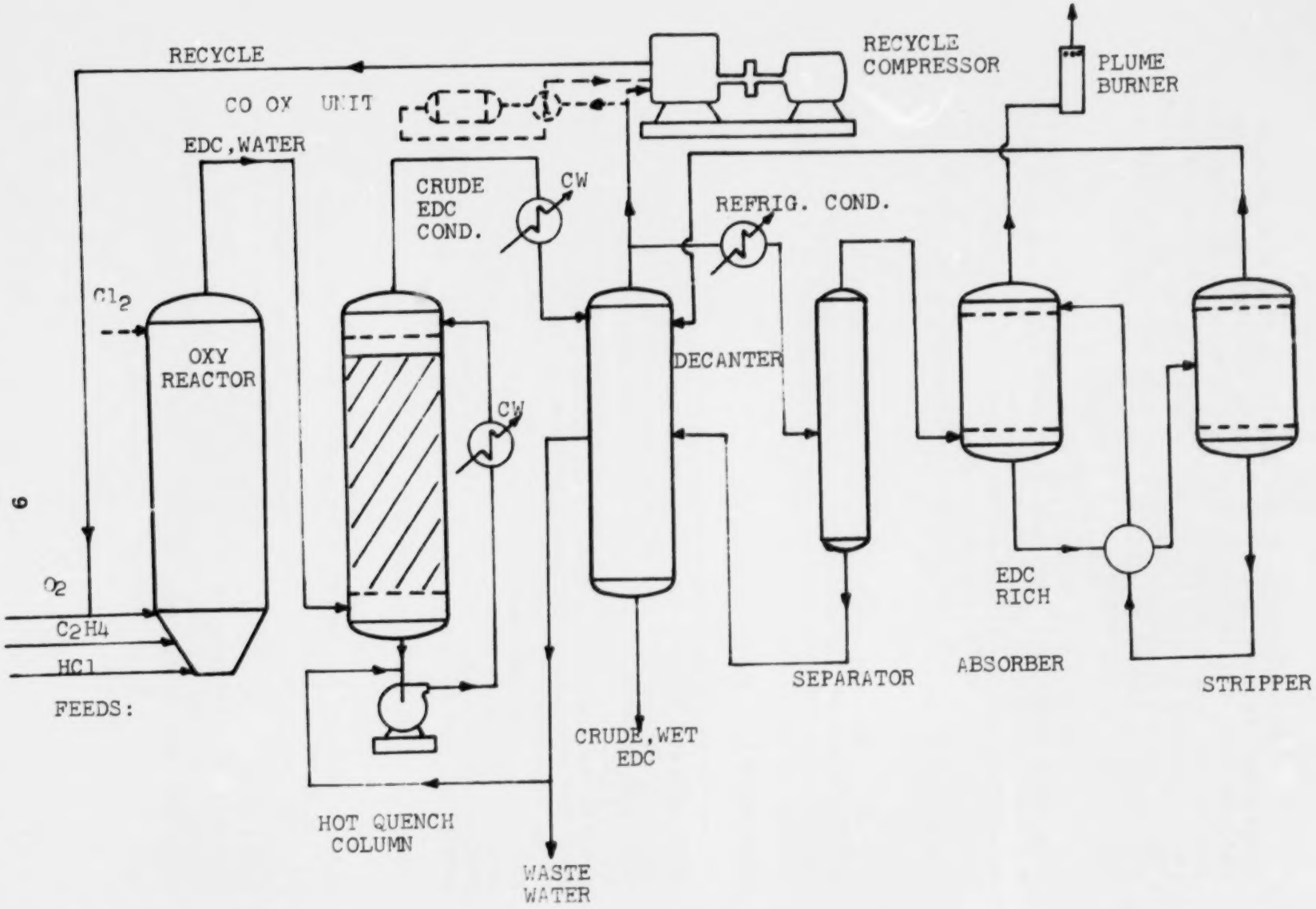


FIGURE 2:
FLOWSHEET FOR PROPOSED ETHYLENE OXYHYDROCHLORINATION PROCESS

The majority of the discharge from the booster compressor is recycled to the oxyhydrochlorinator. This recycle gas will be predominantly carbon dioxide with the process as described here. A small portion of the recycle gas is purged in order to limit the build-up of unreactive impurities which enter the system with the reactor feeds, for example; methane and ethane which are typical impurities in the ethylene.

This purge stream is first cooled in a recuperative heat exchanger and then further cooled in a refrigerated vent condenser which removes most of the ethylene dichloride and ethyl chloride. These are collected in a receiver from which the purge gases, consisting of 80-90% carbon dioxide and 10% methane and ethane, are discharged through the recuperative heat exchanger and may be disposed of via incineration.

The net effect of this process will be at least a 90% reduction in hydrocarbon emissions compared to typical present processes. Thus, the objective and scope of this project can be stated as:

OBJECTIVE AND SCOPE OF PROJECT

The objective of the project was to demonstrate that emissions from the production of ethylene dichloride by oxyhydrochlorination of ethylene could be reduced in a modified process by at least 90% from the levels encountered with typical existing processes. The modified process was to employ recycle of reactor exit gas, oxygen feed and whatever additional processing steps are determined to be necessary to control build-up of by-products in the recycle stream and was to be economically competitive with present-day processes. The process performance was to be evaluated on a laboratory scale and a preliminary study of technical and economic feasibility was to be carried out.

BENEFITS OF SUCCESSFUL EFFORT

The ethylene oxyhydrochlorination vent is the main source of hydrocarbon emissions associated with the manufacture of vinyl chloride. The direct chlorination process produces less than one-tenth of the hydrocarbon emissions of oxyhydrochlorination and cracking of ethylene dichloride, under normal circumstances, produces no emissions. Ethylene dichloride production is stated to account for 28% of the hydrocarbon emissions in the Southern Louisiana and East Texas AQCRs. (5)

There is no practical way of eliminating the oxy-hydrochlorination vent from existing processes; the gases are too dilute for direct incineration and the addition of natural gas to make the gases combustible is an extravagance. Furthermore, incineration will form hydrochloric acid which must be recovered by scrubbing.

The primary anticipated benefit from this project is at least a 90% reduction in hydrocarbon emissions for the proposed process as opposed to presently existing processes, which currently average approximately 0.03 lb hydrocarbons per pound of ethylene dichloride product. It is believed that this can be accomplished with only a modest increase in capital cost and it is anticipated that the benefits of increased raw material yields will off-set this to a great extent.

OUTLINE OF PROJECT

Four major tasks for this project were indicated. The first represented the completion of the cursory study of alternative approaches to reduction of emissions and was required to define in detail the experimental program to follow. The second task represented the point at which the modifications and additions to the existing laboratory oxyhydrochlorination equipment had advanced sufficiently to allow the experimental program for determining the effects of operating conditions to begin. The third task was the point at which the experimental program had advanced sufficiently far to initiate the preliminary technical and economic evaluation of the process. The fourth task was the point at which a recommendation for a future course of action could be made, including, if warranted, preparation of a proposal for a follow-on contract for further development of the process.

The plan of operation consisted of the following tasks, which were directed toward a demonstration of the technical and economic feasibility of the processes:

— Task 1 — Preliminary evaluation of alternative approaches to reduction of emissions from ethylene oxyhydrochlorination.

— Task 2 — Modifications and additions to equipment.

— Task 3 — Determination of the effects of operating conditions on the performance of the existing and proposed processes.

— Task 4 — Preliminary technical and economic evaluation of the proposed process.

The first step in the plan of operation was the preliminary evaluation of the various conceivable approaches to the reduction of emissions from ethylene oxyhydrochlorination. Comparisons with the proposed process were made.

SECTION IV

PRELIMINARY EVALUATION OF ALTERNATIVE APPROACHES

The preliminary evaluation of alternative approaches considered the following process alternatives: oxygen feed with vent gas recycle on the existing process; catalytic oxidation of vent gas; and thermal incineration of the vent gas.

The results of the economic evaluations of these alternatives show clearly that the oxygen addition with vent gas recycle on the existing process is by far the most economic choice. The estimates are based on a 700 MM lb/year EDC plant.

The results can be summarized as shown in Table 1.

Tables 2, 3 and 4 and Figures 3, 4 and 5 illustrate the processes considered and their detailed capital and manufacturing cost considerations.

Two other schemes, compression of vent gas with absorption in a solvent, the adsorption of the hydrocarbons which occur in the vent gas, do not at first look, appear to be worth considering in detail, since initial economic considerations militate against them.

TABLE 1

Economic Consideration	Process		
	Oxy Feed — Recycle	Thermal Incineration	Catalytic Oxidation
Net Capital Increase	($1,300,000)*	$1,750,000	$2,250,000
Net Increase in Manufacturing Cost	$377,000/y	$695,000/y	$985,000/y
Unit Cost Increase, ¢/lb EDC	0.054	0.099	0.141

* Figures in parentheses refer to savings in capital.

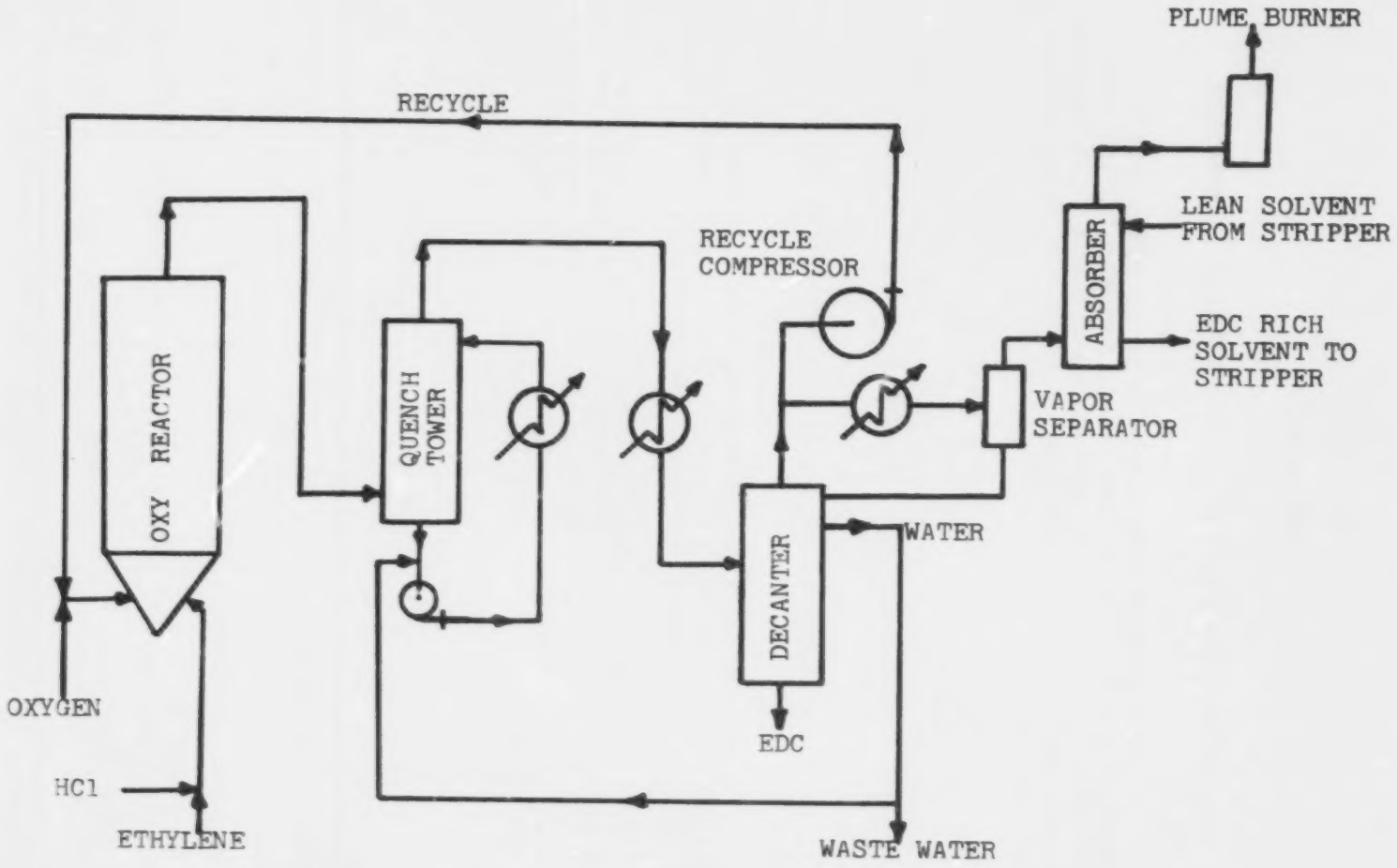


FIGURE 3: CONCEPTUAL FLOW DIAGRAM OF ETHYLENE OXYHYDROCHLORINATION WITH VENT GAS RECYCLE AND OXYGEN FEED

TABLE 2

PRELIMINARY COST STUDY
OHC PROCESS WITH O_2 FEED AND VENT GAS RECYCLE
COMPARISON WITH OLD PROCESS —
AIR FEED AND NO RECYCLE

Fixed Capital:	New Process	Old Process
Air Compressor	$ -	$ 540,000
Recycle Compressor	210,00	-
EDC Recovery System on Off Gas	45,000	180,000
Off Gas Plume	50,000	-
Purchase Cost — Major Equipment	$ 305,000	$ 720,000
Net Saving	415,000	-
Factored Costs	415,000	-
Total Direct Saving	830,000	
Saving in Overhead and Fees	470,000	
Net Capital Increase	(1,300,000)	

Manufacturing Costs:	
O_2 — 65,000 NT at $25	$ 1,625,000
C_2H_4 Credit — 1580 NT at $100	(158,000)
EDC Credit — 2280 NT at $64	(146,000)
Electric Power (Credit) — 27,500 MKWH at $14	(385,000)
Maintenance Credit — 7% of F.C.	(91,000)
Depreciation Credit — 10% of F.C.	(130,000)
Taxes and Insurance Credit — 1% of F.C.	(13,000)
Net Manufacturing Cost	$ 702,000
Return on Investment Credit — 25%	(325,000)
Net Cost Including ROI Credit	$ 377,000
Unit Cost Increase — ¢/lb EDC	0.054

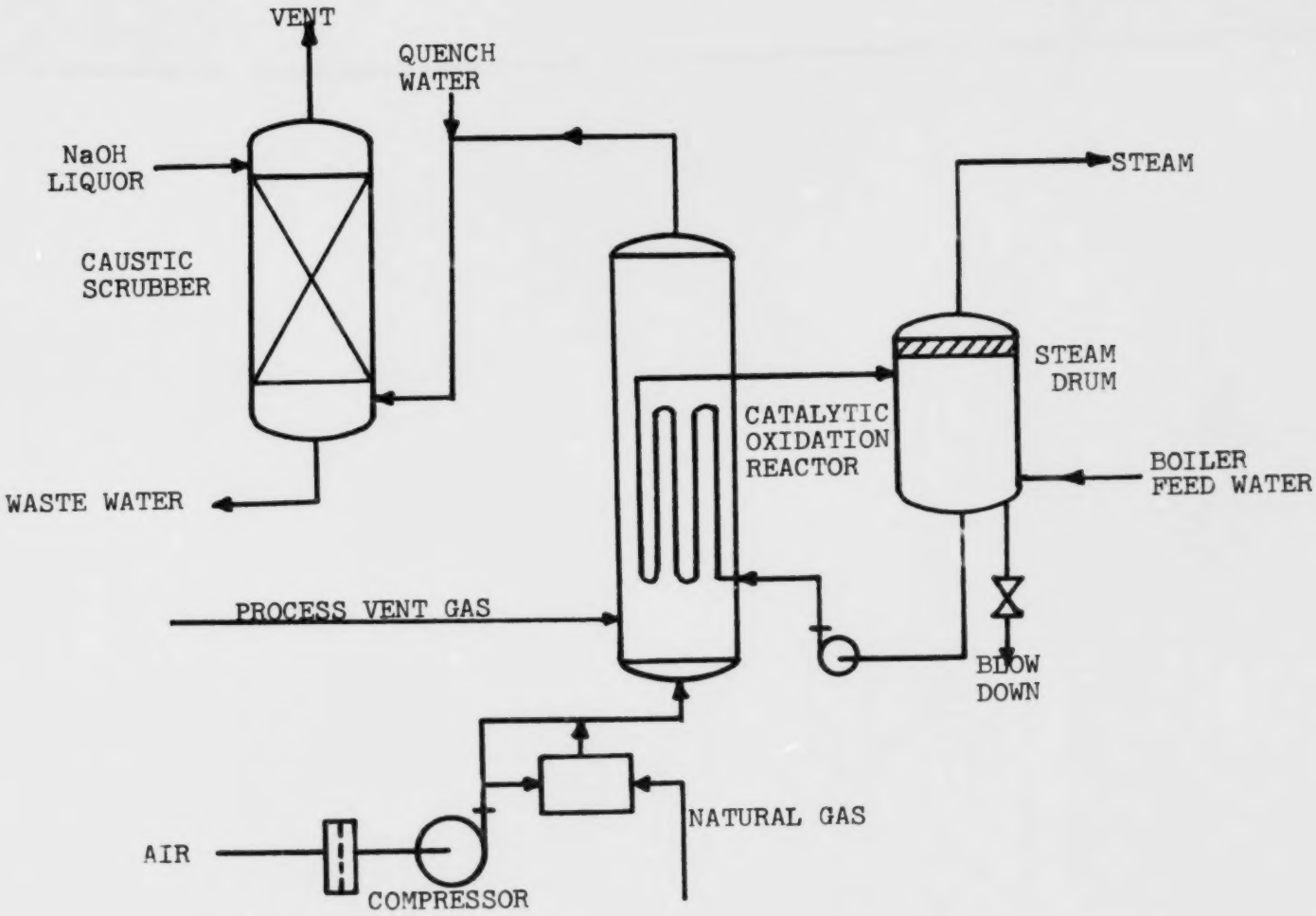


FIGURE 4: CONCEPTUAL FLOW DIAGRAM OF CATALYTIC OXIDATION PROCESS FOR DISPOSAL OF OXYHYDROCHLORINATION VENT

TABLE 3

PRELIMINARY COST STUDY
CATALYTIC OXIDATION PROCESS FOR
VENT GAS DISPOSAL

Capital Cost:	
F.O.B. Equipment Cost	$ 610,000
Factored Costs	765,000
Catalyst	60,000
Sub-Total	$ 1,435,000
Contractor's Fee	$ 70,000
Engineering, Contingency and Overheads	745,000
Grand Total	$ 2,250,000
	$/Year
Manufacturing Costs:	
Labor	$ 22,000
Maintenance, 7% of F.C.	180,000
Supplies	18,000
Catalyst Make-up	60,000
Electricity	120,000
Water	15,000
Caustic Soda	265,000
Steam (Credit) — 144,000 NT at $3.50	(504,000)
Depreciation	225,000
Taxes and Insurance	22,000
Total Manufacturing Cost	$ 423,000
25% Return on Investment	562,000
Total Cost Including ROI	$ 985,000
Unit Cost Increase — ¢/lb EDC	0.141

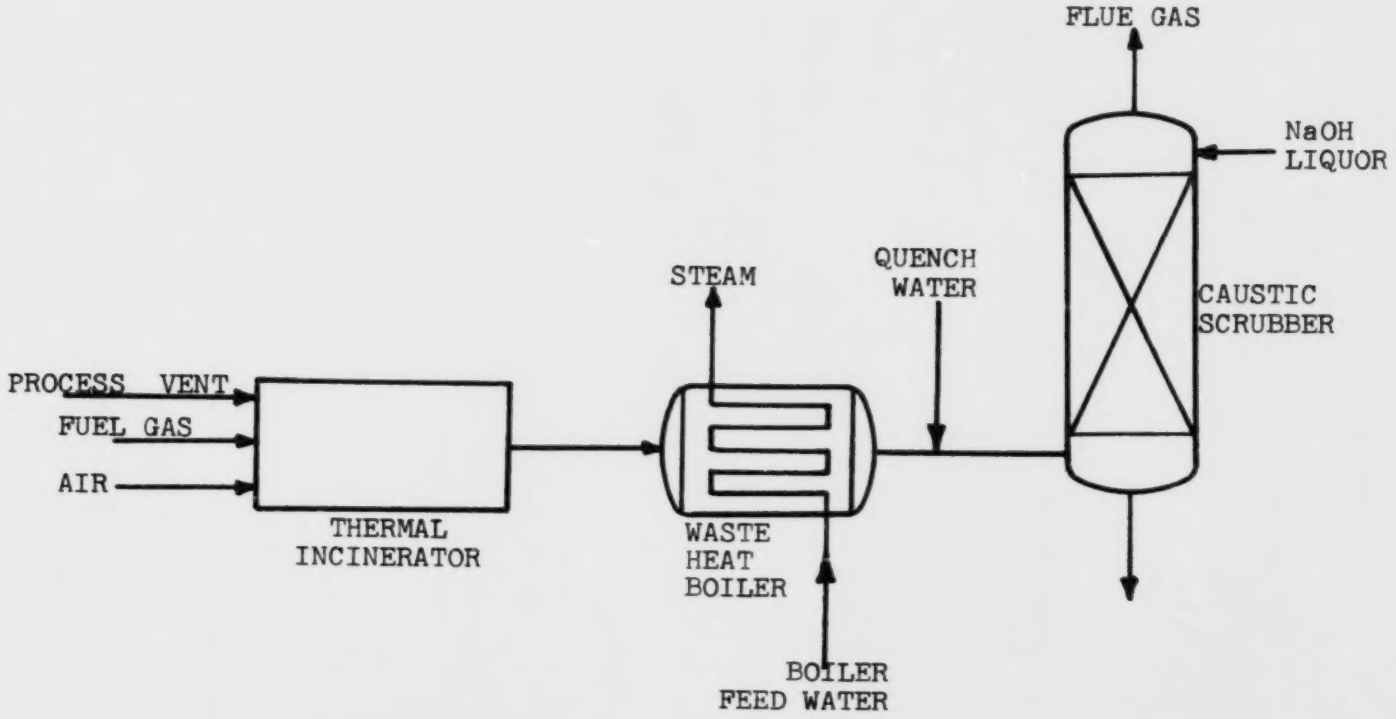


FIGURE 5: CONCEPTUAL FLOW DIAGRAM OF THERMAL INCINERATION PROCESS FOR VENT GAS DISPOSAL

TABLE 4

PRELIMINARY COST STUDY
THERMAL INCINERATION FOR DISPOSAL
FOR OXY VENT GAS

Capital Costs:
(F.O.B. Equipment Costs per Houdry — with Escalation)

Thermal Incinerator	$	105,000
Waste Heat Boiler and Auxiliaries		175,000
Caustic Scrubbing Equipment		215,000
Purchase Cost — Major Equipment	$	495,000
Factored Costs at 125%		620,000
Total Direct Cost	$	1,115,000
Overheads and Fees		635,000
Total Fixed Capital	$	1,750,000

Manufacturing Costs:

Labor	$	22,000
Maintenance — 7% of F.C.		122,500
Supplies		10,000
Fuel — 57,000 MM BTU at $1.15		66,000
Boiler Feed Water		15,000
Caustic Soda — 3305 NT at $80		265,000
Steam Credit — 124,500 NT at $3.50		(436,000)
Depreciation — 10% of F.C.		175,000
Taxes and Insurance — 1% of F.C.		18,000
Total Manufacturing Cost	$	257,500
25% Return on Investment		437,000
Total Cost Including ROI	$	694,500
Unit Cost Increase — ¢/lb EDC		0.099

SECTION V

DESCRIPTION OF EXPERIMENTAL PROGRAM AND EQUIPMENT

EXPERIMENTAL PROGRAM

The development of a successful recycle process which would reduce emissions by at least 90% depended on the answer to several important questions which were best evaluated in a once-through process.

Since the recycle process concept depended for its success on the build-up of inerts (CO_2) in the system to replace nitrogen which was absent due to the use of oxygen instead of air, certain questions needed to be resolved before development of a recycle process and which depended on the chemistry of the process.

The main chemical reactions which occur in fluid-bed oxyhydrochlorination of ethylene are:

Principal Reaction:

$$C_2H_4 + 2\ HCl + 1/2\ O_2 \longrightarrow C_2H_4Cl_2 + 2\ H_2O \qquad (1)$$

Cupric Chloride Catalyst

Main Side Reactions:

$$C_2H_4 + 2\ O_2 \rightleftharpoons 2\ CO + 2\ H_2O \qquad (2)$$

$$C_2H_4 + 3\ O_2 \rightleftharpoons 2\ CO_2 + 2\ H_2O \qquad (3)$$

$$C_2H_4 + HCl \rightleftharpoons C_2H_5Cl \qquad (4)$$

$$2\ CO + O_2 \rightleftharpoons 2\ CO_2 \qquad (5)$$

Questions Needing Resolution Before Final Development of a Recycle Process

Question 1: Will CO build-up in the recycle system reach levels which will cause explosive conditions?

Will the ratio of CO_2/CO remain at about 2 in the recycle system as it does in the once-through system?

Can the reactor system effectively oxidize CO to CO_2?

Question 2: If CO is not oxidized in the reactor, but is oxidized in a separate unit, how do we avoid the loss of ethylene value by oxidation?

Question 3: Can post-chlorination effectively work on the exiting reactor gases to convert unreacted ethylene to EDC?

Question 4: What is the effect of the reactor system on hydrocarbon impurities, such as CH_4 and C_2H_6, which might occur in the ethylene feed?

With these questions before us, the scope of an experimental program was evolved as follows:

Scope of the Experimental Program

1. Once-Through Runs

   (a) Baseline runs at 230-240°C with 5, 10, 15% excess C_2H_4 and 60-70% excess O_2 (as air).
   (b) Runs with CO and CO_2 additions.
   (c) Hydrocarbon additions — CH_4 and C_2H_6.
   (d) Post-chlorination work.

2. Recycle Runs (O_2 Feed)

   (a) Runs at 230, 240, 250°C with 5-20% excess C_2H_4 and 50-115% excess O_2 with vent rates of less than 10% of the total off-gases.

DESCRIPTION OF LABORATORY OHC PILOT-PLANT EQUIPMENT

ONCE-THROUGH SYSTEM

Reference to Figures 1 and 6 will aid in the description of the once-through OHC pilot plant. Although Figure 1 shows an absorber-stripper arrangement which is used in commercial operation, the laboratory version used a refrigerated condenser instead. Also, even though Figure 6 describes the simplified recycle process, the

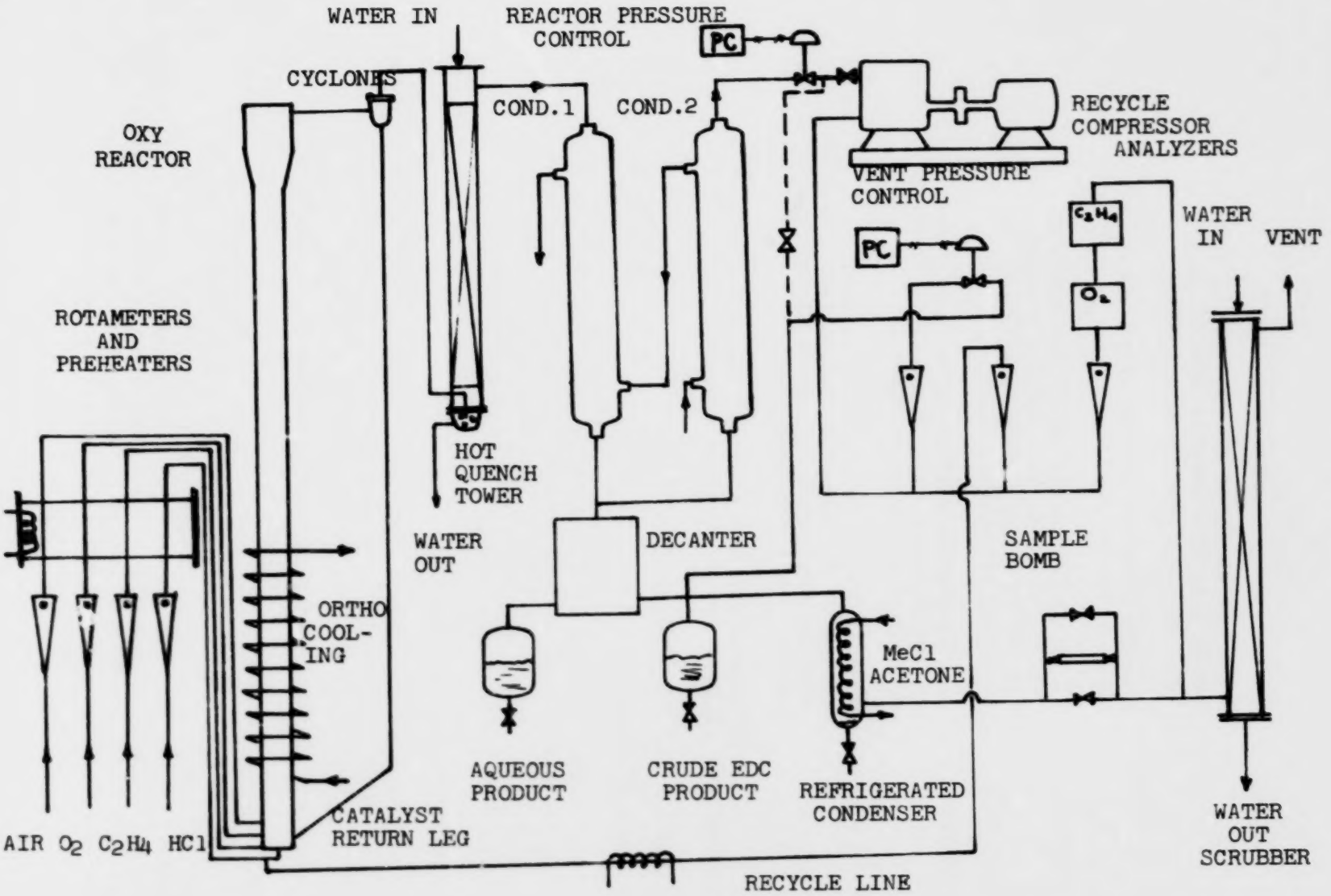


FIGURE 6: SIMPLIFIED FLOWSHEET OF PILOT PLANT OXYHYDROCHLORINATION RECYCLE PROCESS

once-through process can be seen in this diagram by following the dashed flow line after the reactor pressure control valve, thereby by-passing the entire recycle system.

The once-through process begins with the cylinder gas supplies and flow metering equipment. Ethylene used in the process is 99.6% pure or better. HCl is a technical grade which contains some moisture (removed with a $CaCl_2$ drier in the system), and oxygen was a commercial grade with a 99.6% pure or better specification. Flows were monitored at constant temperature and pressure through banks of calibrated Fischer and Porter Tri-Flat rotameters and into individual electrically-heated, stainless steel preheaters (nickel for HCl).

Air or oxygen was fed separately into the bottom of the reactor spool piece and the ethylene and HCl flows were mixed together in a mixing tee at their entrance into the reactor. The reactor consisted of a 2 1/2 inch diameter pipe 15 feet high with a four foot disengaging section of 8 inch diameter pipe at the top. Catalyst was a typical cupric chloride on alumina variety. The reactor had pressure taps and thermocouple locations as illustrated in the detailed flowsheets, Figures 7 and 8. Control of reactor temperature and removal of the heat of reaction was accomplished by a cooling jacket on the lower five feet of the reactor and cooling coils on the next four feet of reactor which utilize Dowtherm E as coolant. The Dowtherm was cooled by means of a water heat exchanger.

Reactor gases passed into a TML Dorrclone to remove catalyst fines (returned via the catalyst return leg) which were necessary for proper fluidization. The hot gases then passed into the bottom of the hot quench tower where they were cooled and scrubbed of unreacted HCl.

The cooled gases then passed to condensers where both EDC (ethylene dichloride) and water are condensed out and flow to the decanter for separation and collection. The non-condensables (O_2, N_2, CO, CO_2, C_2H_4, trace EDC) then flowed through the reactor pressure control valve which regulates the pressure back to the reactor.

The once-through process then passed these off-gases through a methylene chloride-acetone-dry ice cooled refrigerated condenser which operated at $<-40°C$ and which removed residual EDC. Commercially, this is usually accomplished with an absorber-stripper arrangement.

Gas sample bombs could be taken downstream of this refrigerated condenser. Final gases passed to a packed scrubber, the gaseous effluent of which passed to a roof vent.

RECYCLE SYSTEM

Figures 2, 6, 7 and 8 illustrate the recycle system components. The components of the once-through process were utilized directly in the recycle process.

The flow description for the recycle process will be picked up from the reactor pressure control valve since both systems were similar up to this point.

The gases passing through the reactor pressure control valve fed the inlet to the ITT Pneumative, triple piston, single-stage recycle compressor Model SGH71-T. Due to leakage past the pistons*, the compressor was housed in a pressurized enclosure fabricated from 16" steel pipe which was closed at one end with a welded plate and at the other with a blind flange. Pressures between 40-60 psig were maintained by means of a cylinder of CO_2. Flow rates of this CO_2 stream were noted and recorded.

The exit gases from the recycle compressor (60-90 psig) were fed to a bank of three rotameters in parallel. The first rotameter was the vent rotameter which fed the vent pressure control valve. The setting of the controller for this valve determined the vent rate and thus the recycle rate also. The next rotameter was the recycle rotameter which fed back to the reactor bottom (after preheating). The third rotameter was the sample rotameter which controlled flow to the Beckman Model 742 Polarographic oxygen analyzer and the Beckman Model 865 infrared ethylene analyzer. Provision was made (as shown in the detailed flowsheets, Figures 7 and 8) to calibrate each gas analyzer separately with its own gas supply and metering system.

The vent was passed through the methylene chloride-acetone refrigerated condenser to the sample bomb and out to the scrubber.

The complete flowsheets, Figures 7 and 8, give the entirety of the recycle process. The accompanying legend, Table 5, identifies additional components and data monitoring points.

* Only a pilot plant problem; not anticipated to be a problem in industrial operation.

TABLE 5

LEGEND FOR FLOWSHEETS
FIGURES 7 AND 8

A_1 — Low air pressure alarm
A_2 — Low HCl pressure alarm
A_3 — HC in air explosive alarm
A_4 — HC in air explosive alarm

C_1 — CAL-Rod
CO_1 — Recycle gas cooler (for moisture elimination)

D_1 — HCl dryer
D_2 — Sample rotameter filter and dryer
D_3 — C_2H_4 inlet sample filter and dryer
D_4 — C_2H_4 inlet calibration filter and dryer

F_1 — Air filter
F_2 — Purge recycle filter
F_3 — Recycle inlet filter
F_4 — Recycle outlet filter and moisture eliminator

HS — Heat Strip-Reactor Top flange
HT_1 — HCl line heat tape
HT_2 — C_2H_4 line heat tape
HT_3 — Reactor top vent tape
HT_4 — Reactor exit line to quench heat tape
HT_5 — Purge recycle heat tape
HT_6 — Quench water heat tape
HT_7 — Recycle line heat tape

M — Mercury manometer pressure relief leg

P_1 — Ortho-dichlorobenzene-recirculating pump (Dowtherm E)
P_2 — MeCl/acetone circulating pump

RE_1 — Air regulator
RE_2 — CH_4 regulator
RE_3 — CH_4 regulator to calibration set-up
RE_4 — C_2H_4 regulator to rotameter
RE_5 — Recycle regulator
RE_6 — Sample regulator
RE_7 — Secondary C_2H_4 regulator to C_2H_4 rotameter in calibration system
RO_1 — Oxygen rotameter
RO_2 — Air rotameter
RO_3 — Cl_2 rotameter
RO_4 — HCl rotameter

RO_5 — CH_4 rotameter
RO_6 — C_2H_4 rotameter
RO_7 — Ortho cooler (water) rotameter
RO_8 — Quench water rotameter
RO_9 — Vent rotameter
RO_{10} — Recycle rotameter
RO_{11} — Sample rotameter to meters
RO_{12} — C_2H_4 rotameter for sample (C_2H_4 meter) system calibration
RO_{13} — CO_2 or N_2 rotameter for sample system calibration
RO_{14} — C_2H_4 in CO_2 rotameter for sample (C_2H_4 meter) system calibration
RO_{15} — Vent rotameter (after refrigerated condenser and to scrubber)

TEMPERATURE LEGEND

TIR_1 — Reactor top
TIR_2 — Reactor top
TIR_3 — Reactor bed
TIR_4 — Reactor bed
TIR_5 — Reactor bed
TIR_6 — Reactor bottom
TIR_7 — Air/recycle entering reactor
TIR_8 — Reactor bed (reactor temperature-control point)
TIR_9 — Reactor bed
TIR_{10} — Dowtherm jacket
TIR_{11} — Mixing tee — C_2H_4 and HCl
TIR_{12} — Quench tower bottom
TI_{13} — Reactor exit gases
TI_{14} — Product condenser
TI_{15} — Ethylene preheater
TI_{16} — HCl preheater
TI_{17} — Air/recycle preheater
TI_{18} — Reactor top flange
TI_{19} — Non-functional
TI_{20} — Reactor head space
TI_{21} — Reactor bed
TI_{22} — MeCl/acetone to refrigerated condenser
TI_{23} — Acid leg (quench)
TI_{24} — Ortho cooler condensate return
TI_{25} — Quench tower top
TI_{26} — Ortho cooler in
TI_{27} — Ortho cooler out
TIW_{28} — Vent gas to analyzer
TI_{29} — Recycle and vent
TI_{30} — C_2H_4 used in calibration
TI_{31} — Oxygen to reactor
TI_{32} — Oxygen preheater
TI_{33} — Compressor enclosure

FIGURE 7

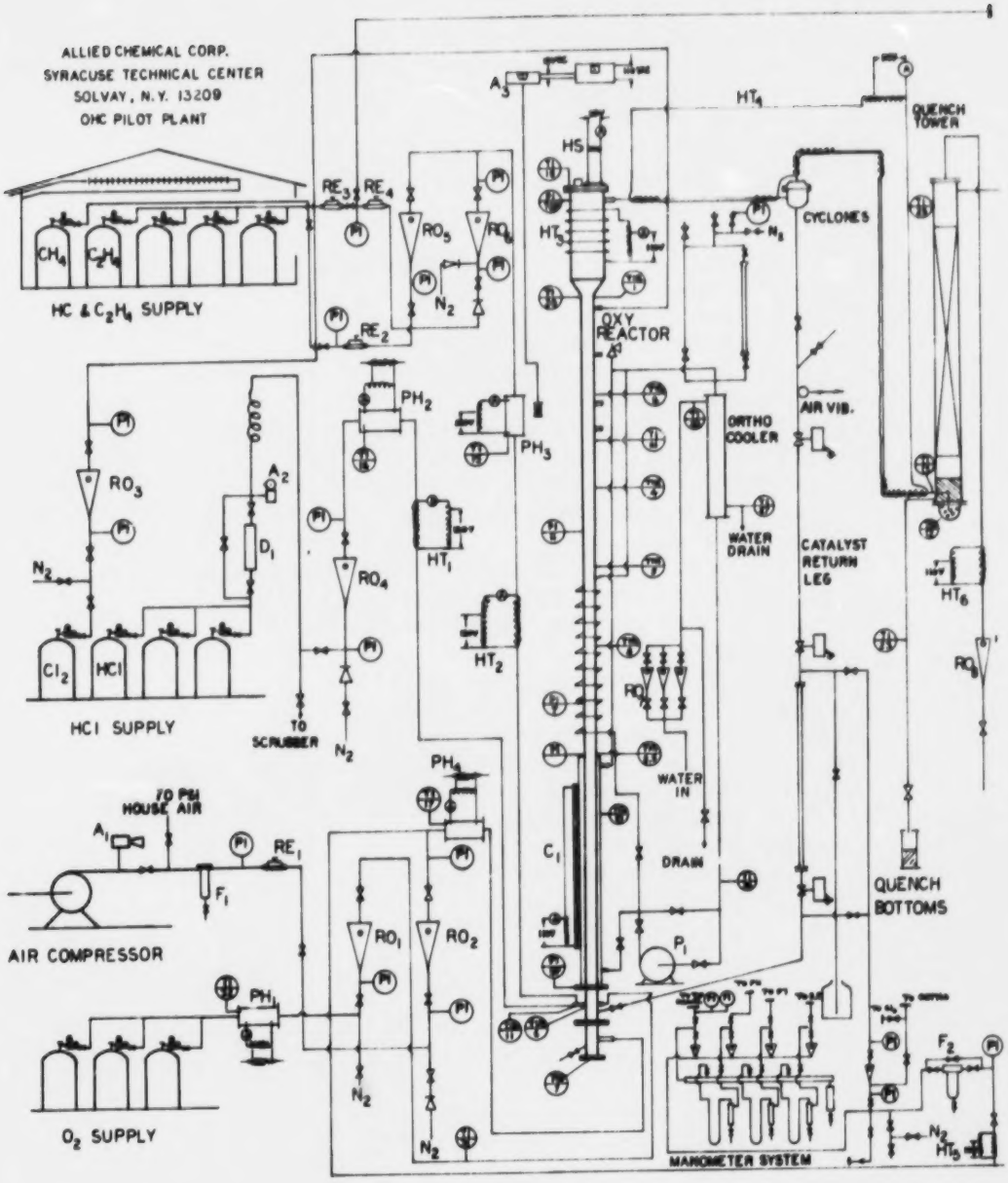

ALLIED CHEMICAL CORP.
SYRACUSE TECHNICAL CENTER
SOLVAY, N.Y. 13209
OHC PILOT PLANT
HC & C_2H_4 SUPPLY
HCl SUPPLY
O_2 SUPPLY
AIR COMPRESSOR
70 PSI HOUSE AIR
TO SCRUBBER
OXY REACTOR
CYCLONES
QUENCH TOWER
ORTHO COOLER
AIR VIB.
WATER DRAIN
CATALYST RETURN LEG
WATER IN
DRAIN
QUENCH BOTTOMS
MANOMETER SYSTEM

FIGURE 7

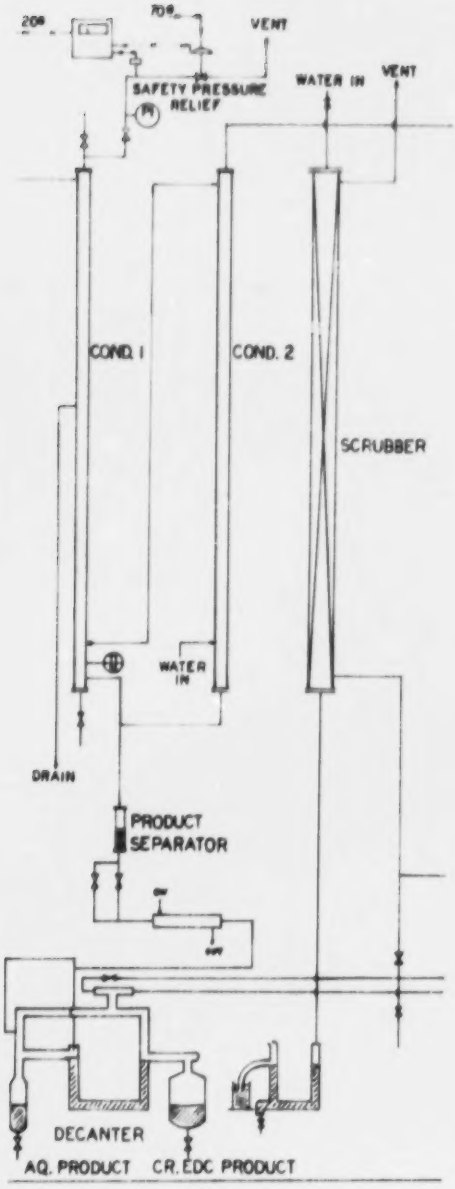

20#
70#
VENT
SAFETY PRESSURE RELIEF
PI
WATER IN
VENT
COND. 1
COND. 2
SCRUBBER
WATER IN
DRAIN
PRODUCT SEPARATOR
DECANTER
AQ. PRODUCT
CR. EDC PRODUCT

FIGURE 8

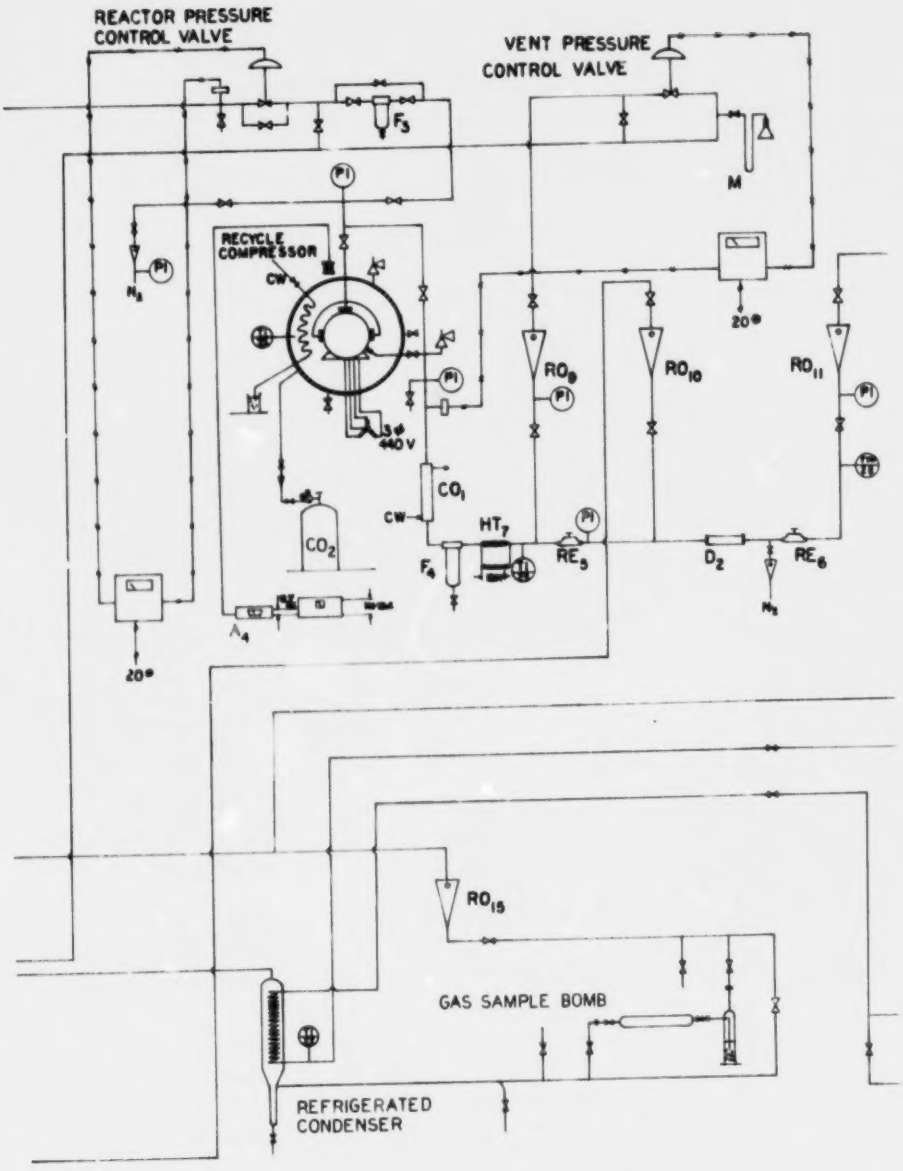
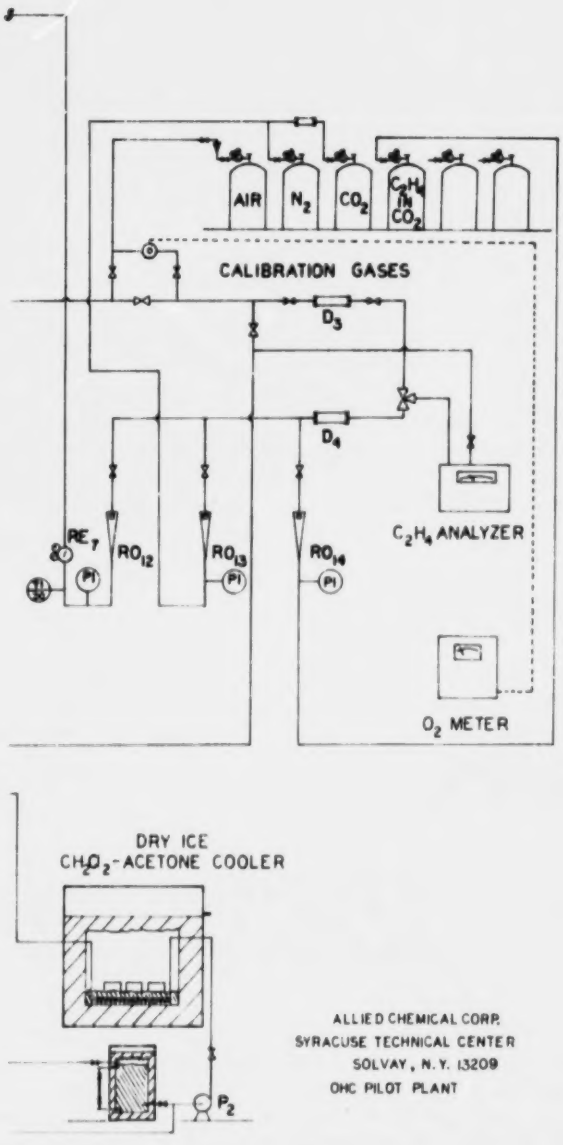

REACTOR PRESSURE CONTROL VALVE
VENT PRESSURE CONTROL VALVE
RECYCLE COMPRESSOR
CW
3ϕ 440V
CO1
CO2
HT7
F4
F3
M
RO9
RO10
RO11
RE5
RE6
D2
A4
20°
RO15
GAS SAMPLE BOMB
REFRIGERATED CONDENSER

FIGURE 8


AIR
N_2
CO_2
C_2H_4 IN CO_2
CALIBRATION GASES
D_3
D_4
RE 7
RO_{12}
RO_{13}
RO_{14}
PI
C_2H_4 ANALYZER
O_2 METER
DRY ICE
CH_2O_2-ACETONE COOLER
P_2
ALLIED CHEMICAL CORP.
SYRACUSE TECHNICAL CENTER
SOLVAY, N.Y. 13209
OHC PILOT PLANT

SECTION VI

EXPERIMENTAL WORK

ONCE-THROUGH PROCESS

The initial work of the once-through process was designed at evaluating baseline emission data. Further work centered around determining the effects of CO, CO_2, CH_4 and C_2H_6 on the reactor system and lastly, the possibility of post-chlorination of reactor gases.

The experimental variables measured for the once-through process are listed, together with all data, in APPENDIX TABLE 1. Of the streams that required chemical analysis were, the vent gas bomb, crude product, aqueous product, and quench bottoms. The results of chemical analysis, together with all flows, were processed in a computer material balance program* to give conversions, yields, efficiencies of all reactants, composition of the vent and waters, and crude product composition. Sampling was done on the basis of one hour periods (with a few noted exceptions). Following will be a discussion of each experimental run, its purpose and its general results.

Experimental Runs

The analytical data for the products of reaction and vent gas analysis are obtained as follows: organic products obtained through gas chromatography; aqueous product and quench bottoms — direct titration for HCl and gas chromatographic analysis for EDC; vent gases — gas chromatography.

Runs 1-5

Runs 1-5 had the function of obtaining baseline data, evaluating catalyst performance, and training operating personnel, together with selection of reactor temperature and pressure.

The runs were organized as follows: Runs 1-5 deal with different excess ethylene ratios, with each run allowing for two operating temperature periods. For example, Run 3 had 10.1% excess ethylene, with 4-1 hour periods of data sampling. The first two periods were at 240°C and the last two were at 230°C. Another variable, excess air, has been

* Available on request from Industrial Environmental Research Laboratory of EPA.

maintained at 60-73% for all runs. The initial baseline data was obtained for 20.0, 16.1, 10.1 and 5.1% excess ethylene.

The vent gas analyses for Runs 1-5 are useful for comparing the Runs 6-8. For all baseline runs, the N_2 is present between 87-91%. CO varies between 0.6 and 1.6%; CO_2 between 1.7 and 4.5%; O_2 between 4.5 and 9%; C_2H_4 between 0.5 and 3.5%; and EDC at about 0.17%. Conversions are typically — for C_2H_4 - 88-99% and for HCl 99-100%. Of the organic product, EDC comprises 98+% of each sample.

Run 6

Run 6 evaluated the effect of pure CO addition in an amount approximately 2 times that which is normally generated within the reactor. This was performed at 5.1% excess ethylene.

Run 6 was performed at 5.1% excess C_2H_4, two temperature levels, viz., 240 and 230°C, 60.3% excess air, and with 2.0 gms/minute of CO added. Run 5, Period 1, shows that the reactor produces 1.13 gms/minute of CO as a reaction product. Run 6, Period 1, which occurs under essentially the same operating conditions shows that 1.14 gms/minute CO is found in the vent gas. This shows that the reactor was able to reduce the injected level of 2 gms/minute to some lesser value in conjunction with the production rate normally occurring in the reactor. The other components of the vent gas, conversions and product yield do not appear to be adversely affected by the CO addition.

Run 7

Run 7 evaluated the effect of pure CO_2 addition in a sizable amount, viz., 5 gms/minute, which is about equal to that normally generated in the reactor operated at 5% excess ethylene.

Run 7 was performed with the addition of 5 gms/minute of CO_2. The purpose of this run was to determine how a higher CO_2 level in the reactor feed affected catalyst, conversions, product distribution, and effluent CO and CO_2 in the vent gas. In Run 7, Period 1, the vent gas contained 6.57 gms/minute CO_2 which is less than the sum of the injected 5 gms/minute plus the normally generated CO_2 in the reactor under identical operating conditions, but without CO_2 addition. These results are summarized below.

Run 8

Run 8 evaluated the effect of pure CO addition, this time, 6-8 times that which is generated normally within the reactor.

Run 8 was performed at the same conditions as Run 6, except that the CO rate was changed to 8 gms/mirute. The vent gas was slightly lower in O_2 and N_2; notably higher in CO; higher in CO_2; and slightly higher in C_2H_4 when compared to Run 5 and Run 6. It was reasonable that the O_2 level should drop since O_2 was used to oxidize CO to CO_2. Also reasonable was the fact that the vent gas was richer in CO and CO_2 since some of the CO from injection was converted to CO_2. The effluent CO was calculated to be 5.75 gms/minute which is again less than that injected (8 gms/minute). Thus, the reactor did reduce the CO level noticeably. The results of the CO runs were encouraging in that they implied that CO oxidation was taking place in the reactor and might therefore negate the need for a CO oxidation unit.

High HCl breakthrough occurred in Run 8 causing reddish brown, iron oxide corrosion product. Run 9 was a baseline run to see if the system had returned to normal operation after this large HCl breakthrough.

Run 9

Run 9 was a standard baseline run with 5.1% excess C_2H_4 and 60.3% excess air with temperatures of 240°C and 230°C. The vent gas, for this run, was about one-half as rich in CO and CO_2 as compared to Runs 4 and 5. This discrepancy is probably due to problems with the catalyst.

Run 10

Run 10 was a run in which 11 gms/minute CO_2 was added to otherwise standard feed streams. The vent gas for Period 2 contained 14.3 gms/minute of CO_2 and was slightly richer in C_2H_4 than without CO_2 addition. The percent conversion for HCl and C_2H_4 remain respectively greater than 99% and 94%. Performance seemed otherwise quite adequate.

Run 11

Run 11 was a CO_2 run at 150 gms/minute imposed on the standard baseline flows. It is equivalent to operating with 63.4% inerts (CO_2 + N_2) or with 32% CO_2. Unfortunately, the run does not give as much information as desired since the superficial velocity was not maintained at the previously set value of 1.2 ft/second but rather 1.77 ft/second. Also, temperature control was not

very good in this run due to the high CO_2 flow. This pointed to the need for a CO_2 preheater or a repiping effort to feed the CO_2 through the air preheater. The vent gas contained 140 gms/minute of CO_2 which shows a net decrease of CO_2 by the reactor. Even with this high CO_2 load, the conversions were still above 99% and 97%, for HCl and C_2H_4, respectively. It is believed that excessive catalyst carryover occurred during this run.

Run 12

Run 12 was a run which returned to the standard baseline conditions, with just reactants and no additional feeds. Again, the vent gas was very low in CO_2 and CO (about 1/2 of Run 5, for example) and indicates a problem in the catalyst bed. The bed was dumped and replaced after this run in order to be sure of good data for the following runs. It was noted however, that percent conversions of HCl and C_2H_4 were quite nominal.

Run 13

Run 13 represented a baseline run with new catalyst. It showed, for example in Period 1, a CO vent gas composition of 0.9% and a CO_2 vent gas composition of 2.2% which are reasonably close to other baseline runs with no problems in the run. Conversions were once again nominal.

Run 14

Run 14 was another CO_2 run, but with O_2 feed instead of air. It was a better indicator of performance than Run 11, since the flows were calculated to maintain the 1.24 ft/second superficial velocity. This run represents 46.3% CO_2 in the feed. Although the CO_2 was preheated, the temperature control on the system was such that the temperatures were a few degress low (236-238°C). Unfortunately, since the vent rate was calculated by using N_2 as the tie substance, and the N_2 contribution was due only to purging, the vent rate is probably not very accurate. There seemed to be no adverse effects to the system from this high CO_2 addition and conversion for HCl and C_2H_4 remained above 99% and 95%, respectively.

Run 15

Run 15 was a CO run with an addition rate of 1.25 gms/minute. The vent gas for all periods for

this run was richer in CO than the feed. For example, Period 1 vent gas had 2.38 gms/minute of CO in it. This can only be explained in terms of a lack of equilibrium within the reactor. At some point, the injected CO must have such a value that the effluent was exactly the same value. Beyond this point, the system reduces the level of CO below its entrance value. Once again the yields were nominal.

Run 16

Run 16 was a high CO run, i.e., 12 gms/minute for Periods 3, 4 and 5, which is more representative of a recycle composition. The effluent in the vent gas was 10.2 gms/minute for Period 4. The other values of vent gas flow of CO gave rates which were all lower than 5 or 12 gms/minute CO, respectively. It appears that the reactor oxidized CO to CO_2, but how efficiently still remained to be answered. The conversions for this run were still within the acceptable range, i.e., 95% and greater.

Run 17

Run 17 represented a baseline run to determine whether the reactor system could be returned to "normal" after the CO addition. The data from that run was within proper bounds when compared to previous similar runs.

At this point, it is well to point out that CO_2 appeared to have no adverse effect on the reaction and that CO was oxidized to CO_2 in the reactor as shown by the data of Table 6. These experiments concluded the tests using CO/CO_2 in the reactor feeds.

Run 18 was designed to study the effect of the reactor on the hydrocarbon gases CH_4 and C_2H_6.

Run 18

Originally, it was proposed to synthesize a recycle gas which would contain CO, CO_2, CH_4, C_2H_6, N_2, O_2, C_2H_4, and HCl. Some of the guiding factors would be: 5% excess C_2H_4, 70% excess O_2, $CH_4/C_2H_6 = 2$, $CO_2/CO = 3$, total inerts = 40%, 40-60% $CO + CO_2$ in $CH_4 + C_2H_6$. Such a mixture, it was believed, would very likely duplicate the feed + recycle stream in the proposed process. It was based on assumptions that CH_4 and C_2H_6 would build up in the recycle stream as a result of impurities in the C_2H_4 feed stream. The figures for CH_4 and C_2H_6 in C_2H_4 feed streams are

TABLE 6

SUMMARY OF CO ADDITIONS RUNS

CO Added in Feed gm/minutes	CO Out in Vent Gas gm/minute	Run/Period
2.0	1.14	6,1
"	1.16	2
"	0.93	3
"	0.75	4
8.0	5.75	8,1
"	5.97	2
"	7.65	3
"	4.10	4
1.25	2.38	15,1
"	2.25	2
"	2.01	3
"	1.95	4
5.04	4.65	16,1
"	4.45	2
12.0	10.6	3
"	10.2	4
"	9.52	5

average and rather high ones at that. Nevertheless, this is what was decided.

In order to guarantee safety, detailed calculations on the flammability limits of the expected vent gas were performed (see References 1, 2, and 3)*. These calculations led to the following results: the lower limit of flammability was found to be 13% and the higher limit of flammability was found to be 43% combustibles. Since the % combustibles in the estimated vent gas would be 37%, the vent gas would be explosive. Such a situation was clearly unacceptable, since the equipment does have glass pipe in the vent legs and general operation under these conditions was not desirable. The only way to deal with this vent gas in this explosive range would be to add N_2 to reduce the combustibles below 13% or to add hydrocarbons to push the combustibles above 43%. Either alternative was expensive and it was decided to use another feed gas mixture.

It was reasoned that high percentages of CH_4 and C_2H_6 in the feed might not occur and also, it was not known whether the reactor system would alter these gases in any way. It was decided for simplicity and ease of operation to return to an air run, i.e., 73% excess air, 9% excess C_2H_4 and use methane as 2% of the feed stream and ethane as 1% of the feed stream (CH_4 = 2.35 gm/minute; C_2H_6 = 2.21 gms/minute). The reactor conditions were as usual, 240°C and 230°C with all other variables the same as previous runs.

The expected vent gas for this mixture was evaluated in terms of its flammability limits with the following results -- lower limit = 65%; upper limit = 76%. Since the percent combustibles would only be 7%, there was no danger of explosion.

The above mixture was run with the following results: vent gas composition (typical); O_2 — 8.6%, N_2 — 81.8%, CH_4 — 4.3%, C_2H_6 — 0.3%, CO — 0.7%, CO_2 — 2.2% and C_2H_4 — 1.9%. This shows that the methane passed through unchanged, but the ethane was reduced by 83% over the inlet value. It can only be supposed that either the ethane was oxidized or chlorinated in some way. This data indicates clearly that methane will build up in the system but that ethane will not. Yields were comparable with previous baseline runs. Table 7 shows the results of CH_4/C_2H_6 additions.

* Composition: 9% CO, 18% CH_4, 9% C_2H_6, 1.5% C_2H_4, 10% O_2, and 52.5% N_2 + CO_2.

TABLE 7

RESULTS OF CH_4/C_2H_6 ADDITIONS

Run/Period	CH_4 Added in Feed gms/minute	CH_4 Out in Vent gms/minute	C_2H_6 Added in Feed gms/minute	C_2H_6 Out in Vent gms/minute
18,1	2.35	2.53	2.21	0.36
2	"	1.97	"	0.37
3	"	2.84	"	0.37
4	"	2.19	"	0.37
5	"	2.57	"	0.36

Runs 19-26 involved post-chlorination of reactor gases, i.e., a total of eight post-chlorination runs were made. Of these, the first three (19, 20, 21) were not quantitative with respect to chlorine analysis of the vent, quench bottoms, or aqueous product. They were used mainly to gain familiarity with the analytical techniques and methods used in the chlorination runs. The computer outputs for these runs are incomplete. One run (#22) was at 12.9% excess ethylene in an effort to see the effect of higher ethylene additions. All other runs were at 8% excess ethylene with chlorine added in an amount which was approximately stoichiometric with respect to the excess ethylene. Runs 19, 20, 21, 22, 23 and 26 had the chlorine injected into the head space above the bed and Runs 24 and 25 had the chlorine injected into the dilute phase of the catalyst bed. It was decided to try both positions since there are valid reasons for doing so. For example, it was reasoned that injection in the dilute phase of the catalyst (lower position) would lead to better conversion since the residence time would be increased, the mixing would be better, and the catalyst should help to promote chlorination. This turned out not to be the case and the details of the comparisons between the two positions was reserved for discussion under Runs 25 and 26.

Analysis of chlorine in the vent was accomplished by bubbling the vent gas through scrubbers containing 0.2 N NaOH. The chlorine in the vent reacts to form hypochlorous acid which can be determined by the standard Iodometric technique (4). The chlorine in the quench and aqueous product were determined directly by the Iodometric method. It was also possible to measure the chlorine dissolved in t he crude product by extracting the crude product with water containing KI, titrating with sodium thiosulfate to a light yellow, adding starch solution, and finishing the determination by a final titration with thiosulfate from a black to a colorless endpoint. This is the Iodometric method adapted to this immiscible system. The usual complete analysis of the crude products was performed together with gas chromatographic work on the vent gas. Thus, it was possible to obtain a close material balance on the chlorine and to use this to speculate on some unsuspected occurrences in these runs.

Runs 25 and 26 are probably the most important of all of the runs. Firstly, they were run as duplicates of other runs, and secondly, they each had a baseline period within the run so that the effect of chlorine addition could be examined in the two following periods for a fixed

temperature (240°C). These runs proved most elucidating and will be discussed below in detail.

Runs 19, 20, 21

These runs were all at 8% excess C_2H_4, 72% excess air with chlorine added in an amount which would approximately chlorinate the excess C_2H_4. Two temperature levels were used: 240°C and 230°C. Quantitative data on chlorine (only) was lacking in these runs. Also, chlorine was injected into the head space. Discussion is deferred to Run 26 (similar to 19, 20, and 21).

Run 22

This run was at 12.9% excess C_2H_4, 72% excess air with chlorine added in an amount which would approximately chlorinate the excess C_2H_4. One temperature level was used: 240°C. If comparison is made to baseline Run #3 (10% excess C_2H_4, 60% excess air) it will be seen that the average vent composition for C_2H_4 was 1.25%. Run 22 showed that the average vent composition for C_2H_4 was reduced to 0.65%. Thus, it can be seen that post-chlorination, in this case, had reduced the ethylene by almost 50%.

Run 23

8% excess C_2H_4, 72% excess air with chlorine added in an amount needed to chlorinate two-thirds of the excess ethylene. Two temperature levels: 240°C and 230°C. See Run 26 for details. This experiment was essentially the same as Run 26, except that Run 26 was only conducted at 240°C. It may be briefly noted that the effect of temperature (10°C difference) was to reduce by 70% the effectiveness of the post-chlorination. Injection was at the top in the head space.

Run 24

Run 24 had 8% excess C_2H_4, 72% excess air with chlorine added in an amount needed to chlorinated two-thirds of the excess ethylene. Two temperature levels: 240°C and 230°C. See Run 25 for details. Injection of chlorine was into the dilute phase of the catalyst. This experiment was essentially the same as Run 25, except that Run 25 was only conducted at 240°C. Here again, the effect of 10°C drop in temperature to 230°C is to increase the ethylene in the vent by 100% when compared to the 240°C run.

Run 25

Run 25 had 8% excess C_2H_4, 72% excess air. This run had the first period as a baseline run with no chlorine, and the last two periods with Cl_2 at 3.66 g/minute. This flow of chlorine would be sufficient to chlorinate 60+% of the excess C_2H_4. Only the 240°C temperature level was used. Such a run was the ideal way to see first hand how the crude product, quench, aqueous product, and vent changed within the same run as Cl_2 was turned on.

The results of this run (made by carefully analyzing Periods 1 and 2 and 1 and 3) lead to the following conclusions:

(a) A total material balance on Cl_2 could not be obtained. That is, approximately 45% of the chlorine cannot be accounted for by analysis of exit streams. The following hypothesis is forwarded. The catalyst is composed of Cu_2Cl_2 and $CuCl_2$ in varying amounts. It is conceivable that we were chlorinating the catalyst by injection of chlorine into the dilute phase of the catalyst. An analysis of the catalyst for Cu^{++} and Cu^{+} has confirmed the shift in the valence of copper ion.

(b) Virtually no chlorine showed up in the vent when injection was into the dilute phase of the catalyst.

(c) Some Cl_2 did show up in the quench and aqueous product under these conditions (none in crude product).

(d) About 53% of the Cl_2 injected was converted to EDC. (Estimated by the increase in EDC product when compared to first baseline period without Cl_2 addition.)

(e) The C_2H_4 in the vent was reduced from 1.14% in Period 1 (no Cl_2) to 0.80% in Periods 2 and 3, about a 30% reduction.

(f) The very high HCl titers in the quench and aqueous product when compared to those when no chlorine was added can be explained by the following scheme: CO in the vent reacted with Cl_2 to form $COCl_2$ (phosgene). $COCl_2$ reacted with water in the quench and aqueous product to form CO_2 and HCl. This HCl, increased very greatly the HCl titer of the quench and aqueous product.

(g) Ethylene conversion was increased by 1.2 percentage points over the case of no chlorination in this run.

Run 26

8% excess C_2H_4, 72% excess air. This run had Period 1 as a baseline run with no chlorine and the last two periods with Cl_2 at 3.67 g/minute. Again, this flow of chlorine would be sufficient to chlorinate 60+% of the excess C_2H_4. Only the 240°C temperature level was used. Such a run was the ideal way to see first hand how the system reacted to the chlorine injection within the same run. Chlorine was injected into the head space.

The results of this run (made by carefully analyzing Periods 1 and 2 and 1 and 3) lead to the following conclusions:

(a) A total material balance on Cl_2 could be obtained to within 3%. It thus substantiates the conclusion of Run 25 that the chlorine was reacting with the catalyst since in this run the chlorine injection was above the catalyst.

(b) Chlorine did show up in the vent in this run. Approximately 25% of the chlorine injected could be seen in the vent.

(c) Larger quantities of Cl_2 were found in the quench and aqueous product than in Run 25; roughly ten times more than in Run 25. Also, a significant amount of Cl_2 was found dissolved in the crude product (about 1% of the injected amount).

(d) Approximately 67% of the injected chlorine reacted to form EDC. This is significantly better than the 53% from Run 25.

(e) The ethylene in the vent was reduced by 75% over Period 1 with no chlorination.

(f) The very high HCl titers were still present in this run as in Run 25 and the same scheme is surmised to apply, viz., the generation of phosgene with the consequent reaction with water to form CO_2 and HCl.

(g) Ethylene conversion was increased by about 1.8 percentage points over the case of no chlorination, in this run.

Thus, it appears that all is not so simple in post-chlorination, and that the better result appears to be achieved at the upper location in the head space due to a competing reaction of Cl_2 with the catalyst at the lower location. Better conversions are apparent at the upper injection port, but Cl_2 does appear in the vent, waters, and crude product and would have to be dealt with especially in regard to corrosion problems.

RECYCLE PROCESS

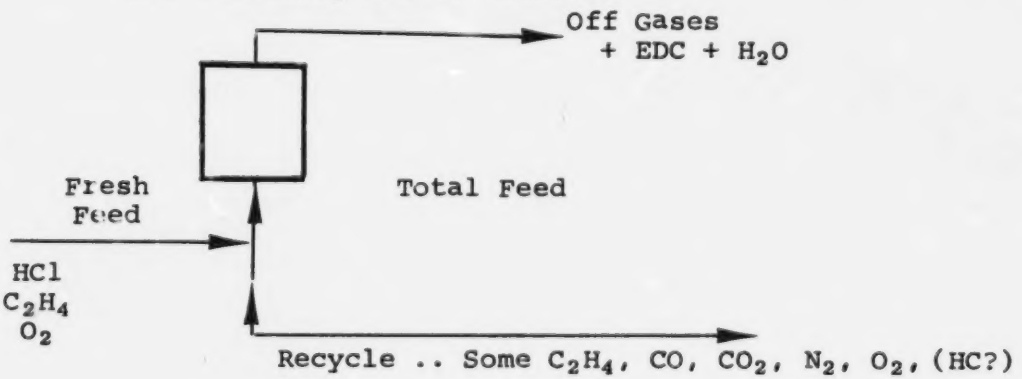
The variables which were important for recycle operation were: (Note: They are not all independent.)

- HCl feed rate — lbs/hr determined capacity of "plant".
- % excess O_2
- Reactor temperature, °C
- Reactor pressure, psig
- Superficial velocity, ft/second
- Recycle rate — mole/time or lbs/time
- N_2 purge rate — needed for proper functioning of pressure taps but also could simulate the N_2 present in commercial 95-99% pure O_2.
- Impurities in the C_2H_4 feed (viz. CH_4 or C_2H_4) or CH_4 additions to simulate such.

Of the above variables, the ones which were not independent (in terms of constant capacity or production and constant temperature) were:

- Reactor pressure, psig
- Superficial velocity, ft/second
- Recycle rate — lbs/time, moles/time

The reasoning was as follows:



For a given feed of HCl in lbs/time or lb moles/time, the capacity or production rate of the system would be fixed. The total feed in lb mole/time, the reactor top pressure, and the superficial velocity would be determined by the reactor cross-section and the ideal gas law. At steady-state, the fresh feed + recycle = total feed. For fixed HCl rate, the amount of O_2 and C_2H_4 in the fresh feed would be determined by the recycle composition and recycle rate. Therefore, the recycle rate will have only one possible value at set conditions of superficial velocity, % excess ethylene and reactor pressure. If we change the reactor pressure, but require that the superficial velocity be maintained constant (along with all other variables), then the only thing which can vary would be the recycle rate. This immediately implies a given vent rate since the production of off-gases would be determined by the HCl rate (capacity). Thus, the amount vented will be fixed at a given fresh feed rate, reactor pressure, % excess C_2H_4, and superficial velocity. Consequently, the emissions will be directly related to this vent rate and its hydrocarbon composition.

The above reasoning then led to the conclusion as to the types of experiments to carry out and the variables to change most easily for experimental work. It appeared that the superficial velocity and recycle rate could be adjusted (i.e., one or the other) while other conditions were maintained constant. In this way, we could develop a set of experiments to be performed.

The analysis of data will be aided by the following idea. One can define an "efficiency", η, which is given by

$$\eta \equiv \frac{\left(E_{HC}\right)_{EX} - \left(E_{HC}\right)_{R}}{\left(E_{HC}\right)_{EX}} \qquad (6)$$

Where $\left(E_{HC}\right)_{EX} = \dfrac{\text{lb Mass of Total Hydrocarbons Emitted}}{\text{lb EDC Produced}}$

in existing once through systems, and

$$\left(E_{HC}\right)_{R} = \frac{\text{lb Mass of Total Hydrocarbons Emitted}}{\text{lb EDC Produced}}$$

in the recycle system.

Clearly, $\eta = 0$ implies that the recycle process is emitting just as much HC/lb EDC produced as the original once-through process. $\eta = 1$ implies no hydrocarbon at all is being vented. The objective of this project was to reduce by 90% the emissions from the existing process. This would correspond to $\eta = 0.9$. Negative values of η would imply that the recycle process is emitting more than the existing once-through process.

In terms of useful graphical plots, it would seem useful to plot η vs. the % recycle rate for constant temperature, pressure, HCl rate, % excess C_2H_4, and % excess O_2. Here percent Recycle Rate = $R/(R + V)$, where V is the vent rate in lb moles/second and R is the recycle rate in lb mole/second. Such a plot should be expected to increase monotonically from $\eta = 0$, $R/(R + V) = 0$ to $\eta = 1$, $R/(R+V) = 1$. The point where $= 0.9$ would yield the minimum recycle rate necessary for 90% reduction of hydrocarbon emissions. It would also be possible to obtain families of curves which would depend on such parameters as reactor temperature, % excess ethylene, and % excess oxygen. Thus, operating data of flow rates, feed compositions, and reactor conditions would indicate where emissions would be more than 90% reduced.

Also useful would be plots of emissions in kg(HC + EDC)/kg HCl vs. % excess C_2H_4 with reactor temperature as parameter. Plots such as this for both once-through and recycle would then enable the plotting of η vs. % excess ethylene with reactor temperature as parameter.

The choice of final operating conditions will always depend on the determination of the best economics. As in the once-through runs, the quench bottoms, aqueous product, crude product, and the vent gas were analyzed. Operating Data and Calculated Data for the recycle process are shown in Tables 2 and 3 in the Appendix.

It will be seen that all recycle runs were conducted at 10 lb/hour HCl with 45 psig reactor pressure and 223°C to 252°C reactor temperatures. Also, all runs had 90% or greater of the off-gases recycled. Superficial velocities were maintained at 1.1-1.2 feet/second. Processing of the data was effected by means of a computer material balance program*. Sixteen recycle runs were made, most with four periods of one hour each. One of these runs was a standard once-through run which was performed to verify the system's consistency.

* Results available on request from Industrial Environmental Research Laboratory of EPA.

Table 8 gives the outline of the recycle experiments conducted in this work.

TABLE 8

Outline of Experimental Runs Obtained on Low Emissions Oxyhydrochlorination Recycle Operation with Oxygen Feed

(All at 45 psig Reactor Pressure, 1.2 ft/sec Superficial Velocity and 10 lbs/hr HCl Rate.)

Run #	Number of Periods	Temperature Range, °C	% O_2 in Vent (O_2 Meter)	Approximate % xs O_2 to Reactor	% C_2H_4 in Vent (C_2H_4 Meter)	Approximate % xs C_2H_4 to Reactor
R100	2	244-246	5.3-7.6	57-83	5.3	14-22
R101	4	242-250	0.23-3.9	52-83	0.7-1.0	5-8
R105	1	242	2.7-3.9	68	1.0-1.1	0
R106	2	241-243	2.4-6.0	60-77	1.4-2.0	10-11
R107	4	241-244	0.34-1.15	75-86	3.4-4.9	16-31
R108	4	239-244	0.75-1.4	56-95	1.4-2.0	11-12
R109	4	240-243	4.2-9.1	71-115	0.95-1.40	9-13
R110	4	249-251	0.26-0.53	68-74	0.65-1.5	10-13
R111	3	251-254	4.6-7.2	100-110	0.6	12

TABLE 8
(Continued)

Outline of Experimental Runs Obtained on Low Emissions
Oxyhydrochlorination Recycle Operation with Oxygen Feed

(All at ~45 psig reactor pressure, 1.1-1.2 ft/second Superficial Velocity, and 10 lbs/hour HCl Rate.)

Run #	Number of Periods	Temperature Range, °C	% O_2 in Vent (O_2 Meter)	Approximate % xs O_2 to Reactor	% C_2H_4 in Vent (C_2H_4 Meter)	Approximate % xs C_2H_4 to Reactor
R112	3	251-252	0.22-0.36	76-78	2.5-3.3	17-20
R113	4	230-231	6.9-8.2	55-74	3.4-3.7	12
R114	4	230-232	0.22-0.36	60-71	2.8-3.4	9-13
R115	1	238	6.6	83	1.2	8.4
R116	4	229-232	2.1-6.1	49-78	3.4-4.8	14-19
R117*	4	230-242	5.3-7.0	70.1	0.6-1.6	5.3
R118	1	223	12.6	77.9	3.4	4.6

* Baseline Run — Once-through Operation

SECTION VII

RESULTS

ONCE-THROUGH PROCESS

Figure 9 shows how wet EDC purity — wt.% varied with reactor temperature. This inversely linear behavior indicates that lower reactor temperatures will be more attractive economically since purification costs will be lessened. The least squares fit of this data is given by:

$$EDC_O = 112.31 - 5.78(10^{-2})\,T \qquad (7)$$

Where EDC_O = Wet EDC purity — Once-through in wt.%
T = Reactor temperature, °C

The standard error of estimate for (7) is 0.226.

Figure 10 shows the kg(HC + EDC)/kg HCl vs. % excess ethylene with reactor temperature as parameter. The fitting lines were obtained by the following procedure: all emission data for the once-through process (at all temperatures) were fit vs. % excess ethylene. This yielded a slope for all the data. Then, this slope was used to re-fit the data at the two temperature levels of 230°C and 240°C vs. % excess ethylene. In this way, consistent correlating lines could be obtained with temperature as parameter.

The results of correlation of emissions data from the once-through process are:

$$\text{(Mean - 231°C)}\quad EM_O = 2.47(10^{-2}) + 1.35(10^{-3})\ XSETH \qquad (8)$$

$$\text{(Mean - 240°C)}\quad EM_O = 1.32(10^{-2}) + 1.35(10^{-3})\ XSETH \qquad (9)$$

Where

EM_O = Emissions in $\frac{\text{kg(HC + EDC)}}{\text{Kg HCl}}$ for once-through operation.

XSETH = Percent excess ethylene to reactor.

FIGURE 9:
WET EDC PURITY-WT%
(ONCE-THROUGH PROCESS)
VS.
REACTOR TEMPERATURE °C

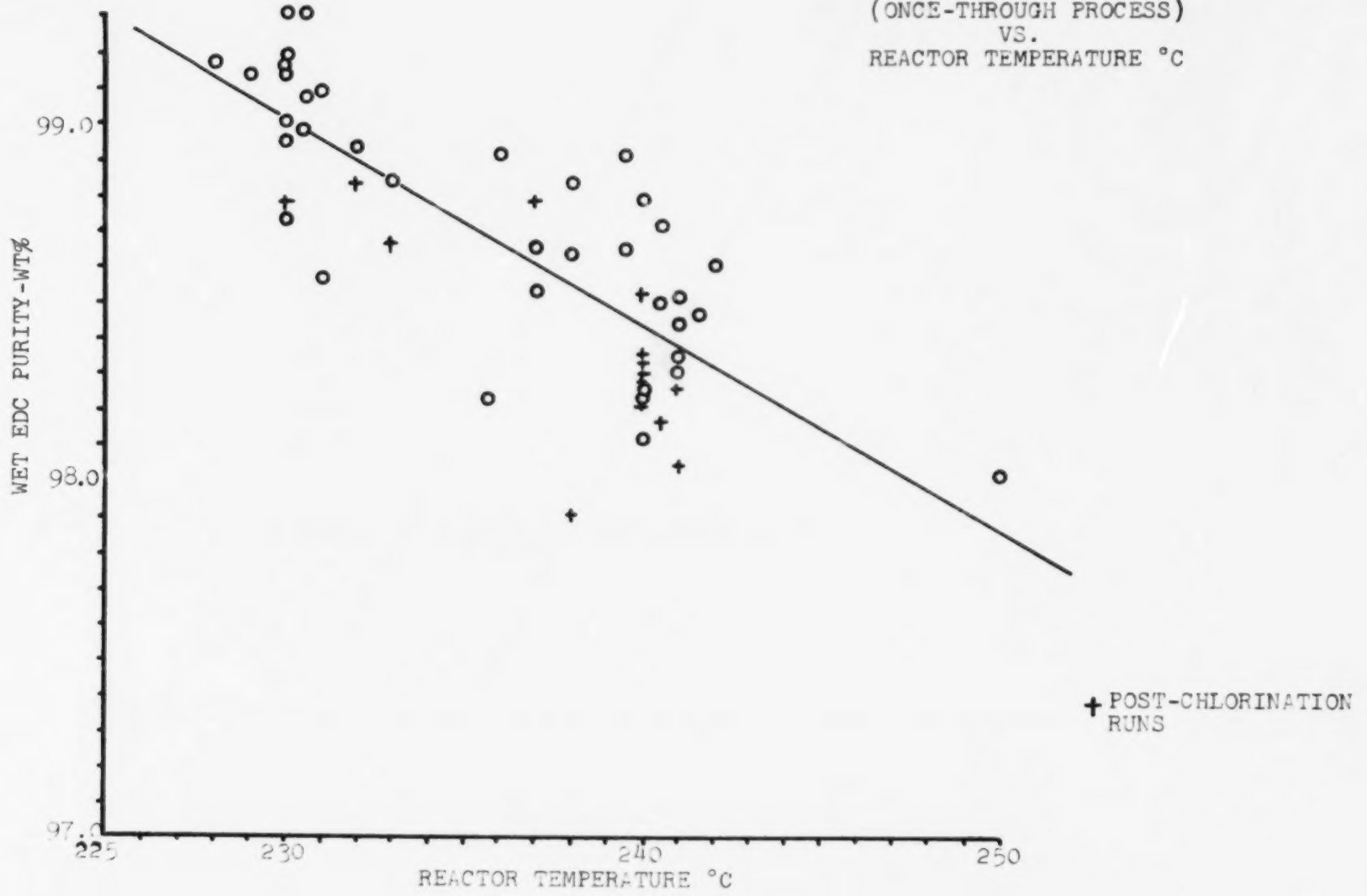
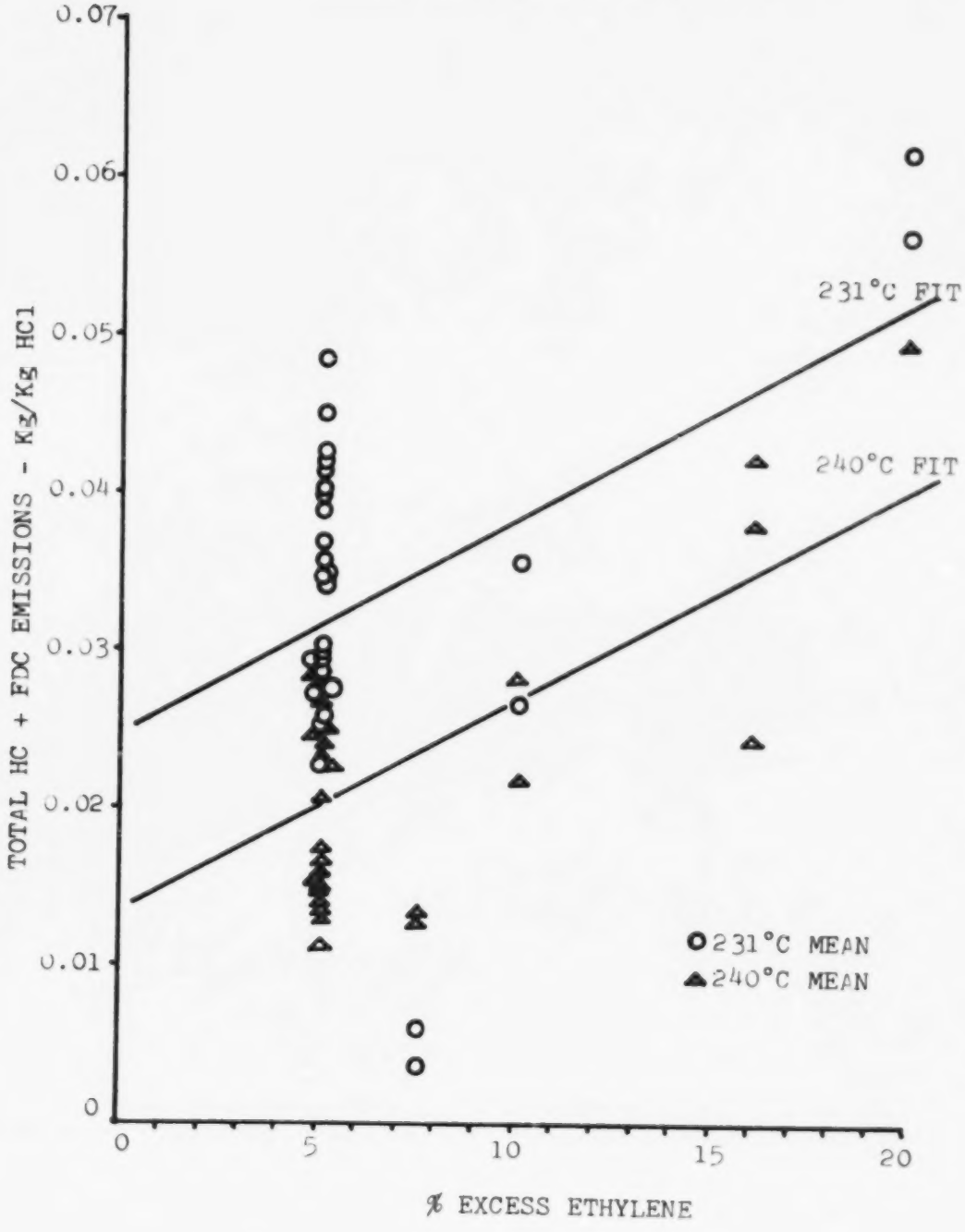


FIGURE 10:
TOTAL HC + EDC EMISSIONS
Kg/Kg HCl
VS.
% EXCESS ETHYLENE (ONCE-THROUGH)
WITH
REACTOR TEMPERATURE AS PARAMETER



RECYCLE PROCESS

Figure 11 illustrates the variation of wet EDC purity (wt. %) with reactor temperature. Again, the purity varies inversely with temperature. Also plotted is the least squares line for the once-through process. Thus, it can be seen that the product purity in the recycle operation is a few tenths of a percentage point lower than the once-through purity at the same temperature. This fact should be taken into account in any economic considerations.

The correlating least squares line for EDC purity is given by:

$$EDC_R = 109.6 - 4.91(10^{-2})\ T \qquad (10)$$

Where EDC_R = Wet EDC purity — wt. % in recycle operation
T = Reactor temperature, °C

Standard Error of Estimate = 0.232

Figure 12 is the correlation of emission data, kg(HC + EDC)/kg HCl vs. % excess ethylene with reactor temperature as parameter. Once again, all the emission data was fit vs. percent excess ethylene (for all temperatures) to obtain a slope for all the data. Then, the slope was fixed and the data for the three temperature ranges — 230, 240, 250°C — was re-fit vs. % excess ethylene. This yielded consistent correlating lines with temperature as parameter.

The results of correlation of emission data from the recycle process are:

(Mean - 230°C) $EM_R = -1.08(10^{-4}) + 2.05(10^{-4})$ XSETH (11)

(Mean - 242°C) $EM_R = -6.45(10^{-4}) + 2.05(10^{-4})$ XSETH (12)

(Mean - 251°C) $EM_R = -8.03(10^{-4}) + 2.05(10^{-4})$ XSETH (13)

Where

EM_R = Emissions in $\frac{Kg(HC + EDC)}{Kg\ HCl}$ for recycle operation.

XSETH = Percent excess ethylene to reactor.

FIGURE 11:
WET EDC PURITY-WT%
VS.
REACTOR TEMPERATURE °C
(RECYCLE DATA)

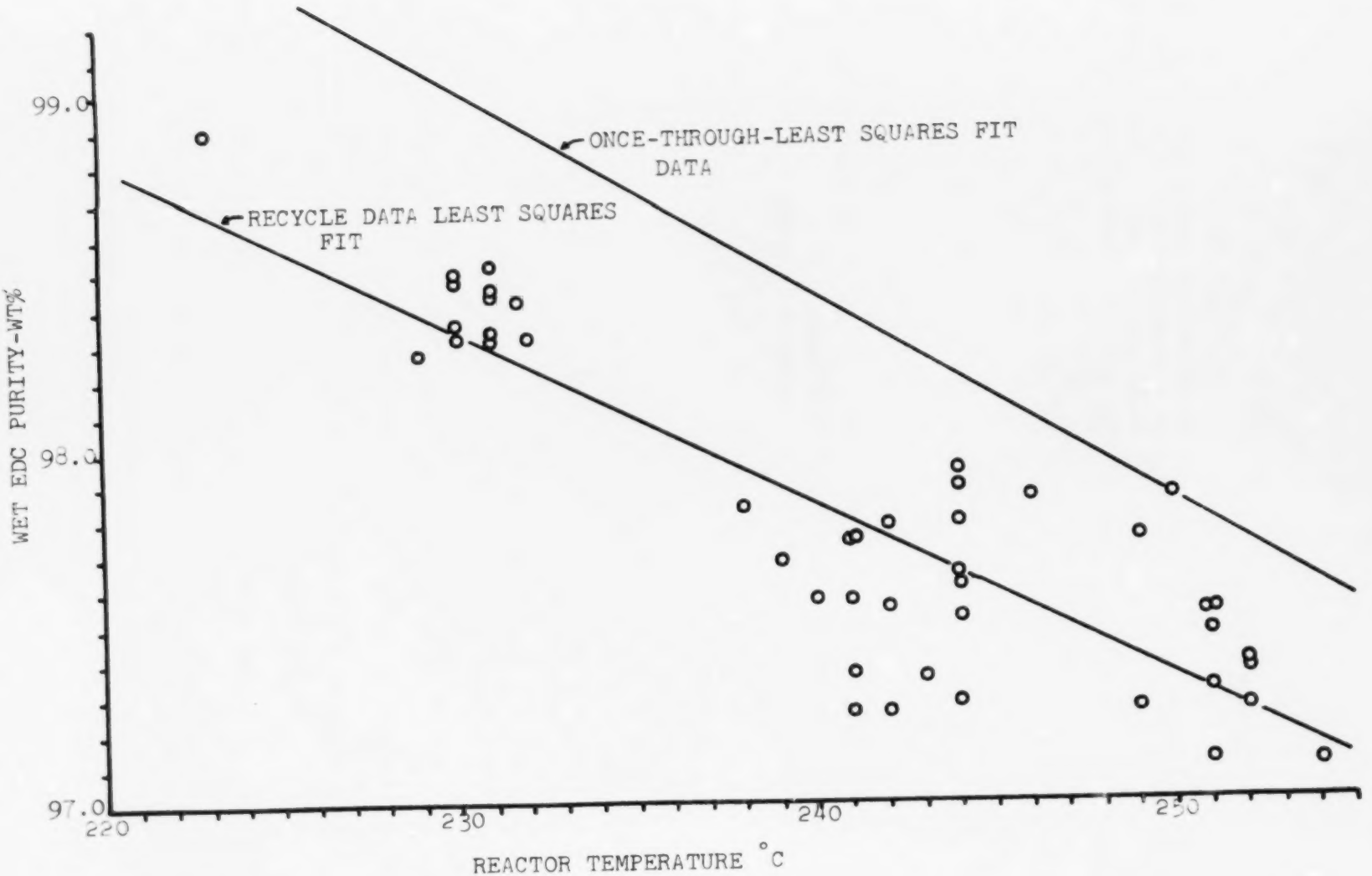
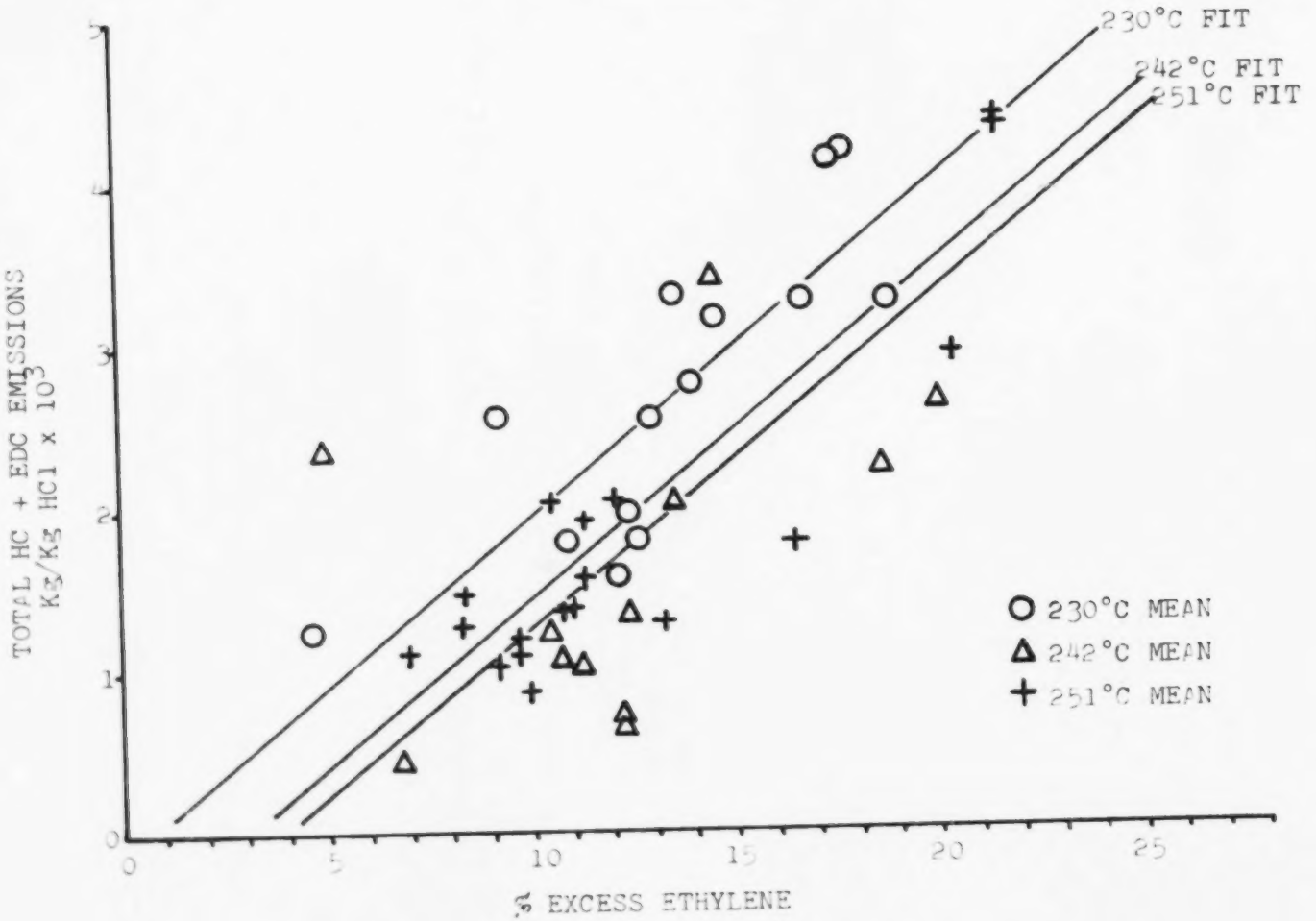


FIGURE 12:
TOTAL HC + EDC EMISSIONS - Kg/Kg HCl
VS.
% EXCESS ETHYLENE
WITH
REACTOR TEMPERATURE AS PARAMETER
RECYCLE PROCESS



COMPARISON OF EMISSIONS FROM ONCE-THROUGH AND RECYCLE

If one compares the emissions from the once-through and recycle operation at the same reactor temperature and percent excess ethylene, the following table results:

TABLE 9

COMPARISON OF EMISSIONS DATA
RECYCLE AND ONCE-THROUGH

Table entries show % reductions in emissions -η of recycle process compared with once-through process at similar values of % excess ethylene and reactor temperature, T°C.

% Excess Ethylene	230°C	240°C
5	97.2	97.4
10	95.1	94.2
15	93.6	92.3
20	92.4	91.1

This result is also shown in Figure 13. Thus, it can be seen that the original objective of this investigation, viz., the reduction by 90% of the emissions from the EDC process through implementation of a recycle scheme has been positively demonstrated.

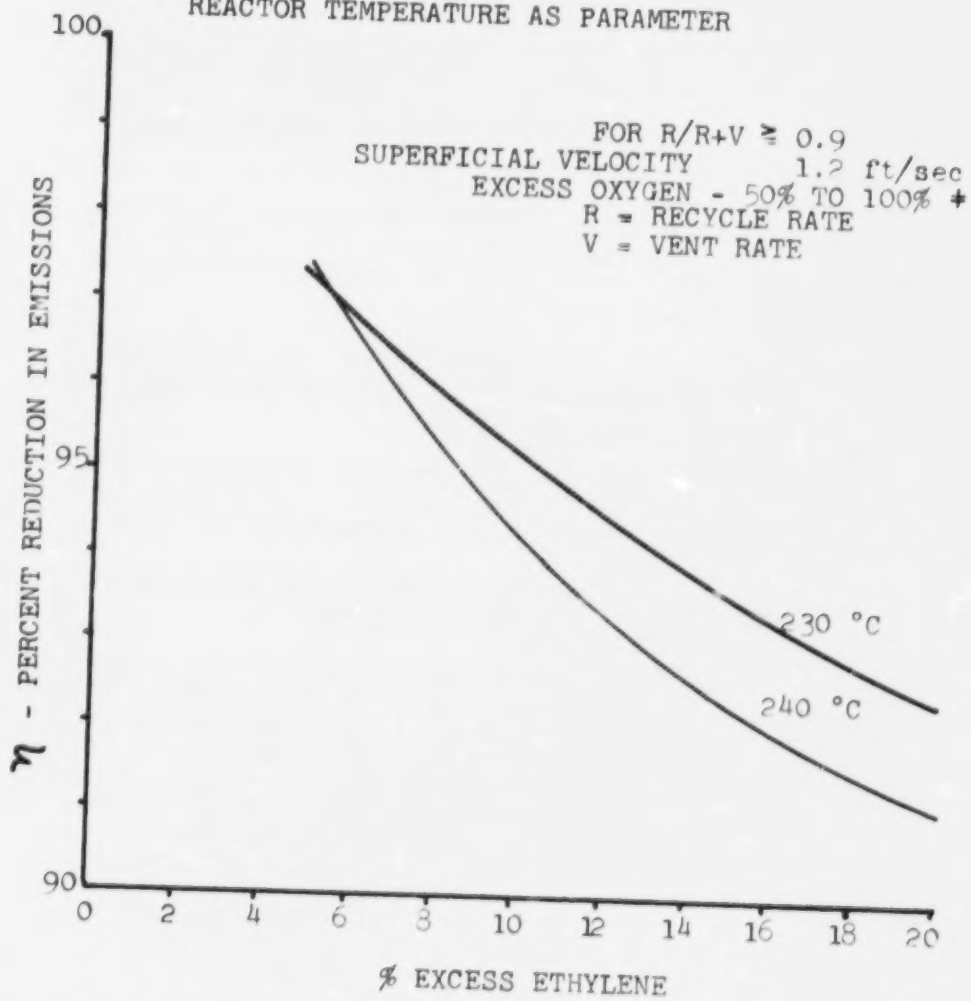
SELECTION OF OPTIMUM OPERATING CONDITIONS

The following trends and facts were used in the selection of the optimum operating parameters:

(a) Crude product (EDC) purity varies in a linearly inverse manner with reactor temperature, i.e., a lower operating temperature yields higher crude EDC purity.

(b) It appears that the crude EDC purity for the recycle operation lies a few tenths (0.5-0.7) of a percentage point below the crude EDC purity for once-through operation at any temperature.

FIGURE 13:
η - PERCENT REDUCTION IN EMISSIONS
RECYCLE COMPARED TO ONCE-THROUGH
VS.
% EXCESS ETHYLENE
WITH
REACTOR TEMPERATURE AS PARAMETER



‡ Most commercial plants operate at 50-70% excess air and 5-10% excess C_2H_4.

(c) Ethylene efficiency decreases with higher operating temperature. Efficiency is defined as

C_2H_4 Converted to EDC/C_2H_4 Fed.

(d) Ethylene efficiency for the recycle process is higher than for the once-through process due to the reduced loss of ethylene in the vent. So also is the oxygen efficiency.

(e) All runs involved recycling greater than 90% of the off-gases.

(f) The comparison between emissions from the once-through process and the recycle process requires a matching of respective operating conditions.

(g) It appears that 230°C forms the lower bound of temperature for trouble-free running of the recycle system.

(h) The minimum excess ethylene consistent with ease of operation, catalyst fluidization, and HCl breakthrough appears to be 5-7%.

(i) The minimum excess oxygen consistent with (h) appears to be about 50%.

The selection of optimum operating conditions in light of the above became dependent on ease of operation and on the conditions which maximized purity and ethylene efficiency. Thus, we found that the minimum in terms of operating costs will occur at the lower temperature boundary of our operating range, viz., at or around 230°C with 5-7% excess ethylene and with 50-60% excess oxygen.

SECTION VIII

COMPUTER SIMULATION AND ECONOMIC STUDY

COMPUTER SIMULATION

In an effort to have a rational method for scale-up of the results from the pilot plant work to a size representative of a commercial unit, a simulation computer program was developed.

The program consisted of a cyclical material balance scheme which utilized experimentally observed gas generation rates within the pilot plant recycle system (i.e., for CO, CO_2). The program had the capability of adjusting feed rates, reactor pressure and temperature, % excess ethylene, % excess oxygen, and the superficial velocity in the bed. Also, by varying the holdup time in the recycle system, various approaches to steady state could be achieved. The output consisted of the recycle rate, vent rate (both in kg mol/hour), % recycled, HC + EDC emissions in kg/kg HCl and the complete vent composition.

As an illustration of the effectiveness of this program in duplicating results, Table 10 is presented. The close correspondence of the simulation to the laboratory data is apparent.

An added feature of the program was the ability to imput CH_4 and/or C_2H_6 in the feeds to simulate their effect on the vent. Data obtained on the once-through process was used to estimate the reactor's effect on C_2H_6. The effect of CH_4 in the feed C_2H_4 and C_2H_6 in the feed C_2H_4 on the % HC emission reduction is shown in Figures 14 and 15, respectively.

Figure 14 shows that CH_4 can create a problem by building up in the recycle stream. In fact, 0.5% or greater CH_4 in the C_2H_4 feed would cause the HC emissions reduction to slip below 90%. The project objective is to maintain at least 90% reduction. The worst case economically (actually used below) is that the vent gas contains CH_4, but not enough to be flammable without the addition of natural gas. Percentages of methane in the feed greater than 2% are already flammable by mixing with air and thus can be flared quite easily.

TABLE 10

COMPUTER SIMULATION

Reactor Temperature ----- 230.6°C
Reactor Pressure -------- 44.9 psig
Superficial Velocity ---- 1.141 ft/sec
Excess Ethylene --------- 13.8%
Excess Oxygen ----------- 63.6%

	Laboratory Data	Simulation
Recycle Rate (KG mol/hr)	0.1695	0.168
Vent Rate (KG mol/hr)	0.0074	0.0077
% Recycled	95.82	95.58
HC and EDC Emissions (KG/KG HCl)	0.0022	0.002
Vent Composition (%)		
O_2	5.16	6.74
N_2	13.98	2.22
CO	2.01	2.035
CO_2	75.17	84.89
C_2H_4	3.13	3.61
C_2H_6	0.10	0.095
EDC	0.46	0.40
$N_2 + CO_2$	89.15	87.11

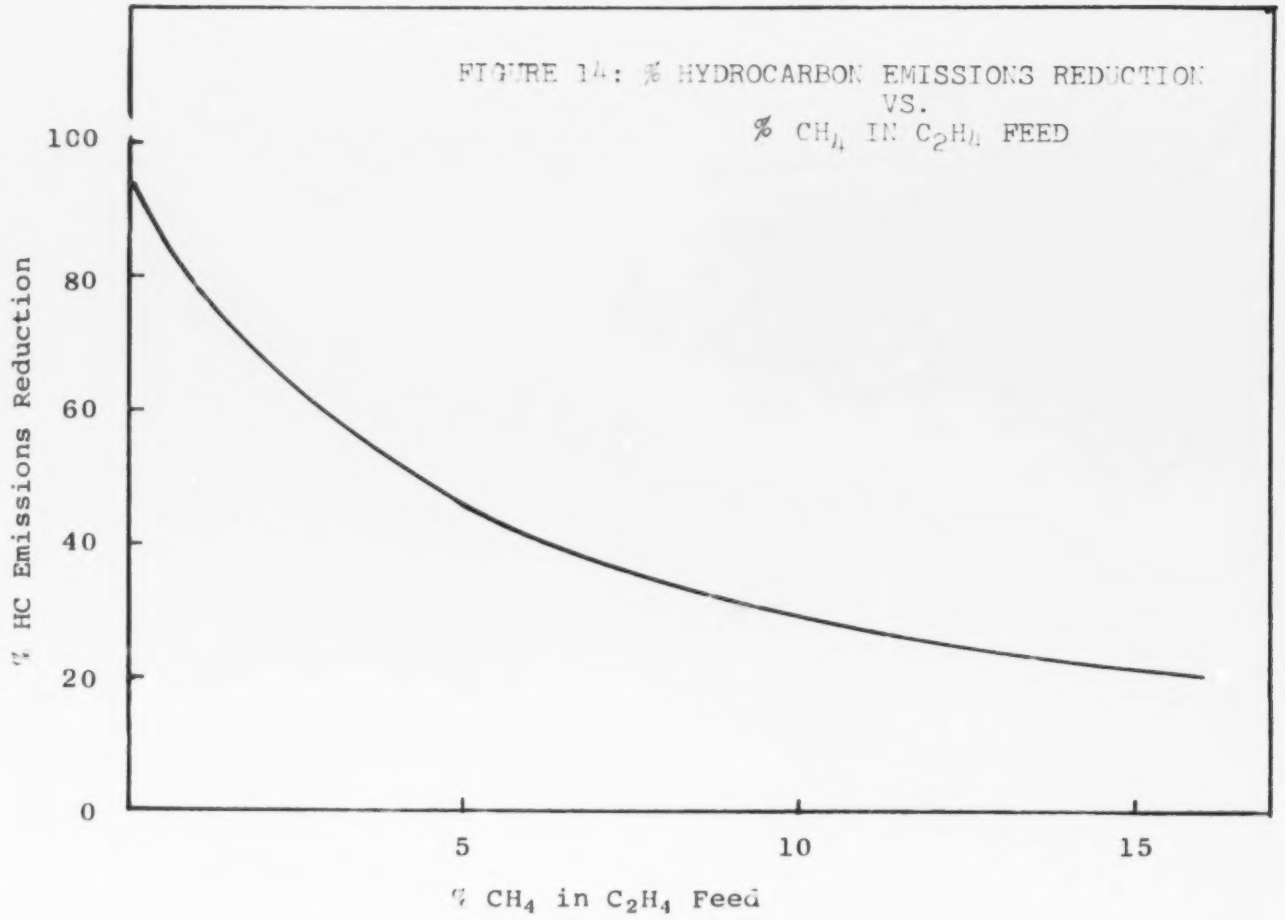


FIGURE 14: % HYDROCARBON EMISSIONS REDUCTION VS. % CH_4 IN C_2H_4 FEED

FIGURE 15: % HYDROCARBON EMISSIONS REDUCTION VS. % C_2H_6 IN C_2H_4 FEED WITH OXYGEN PURITY AS PARAMETER

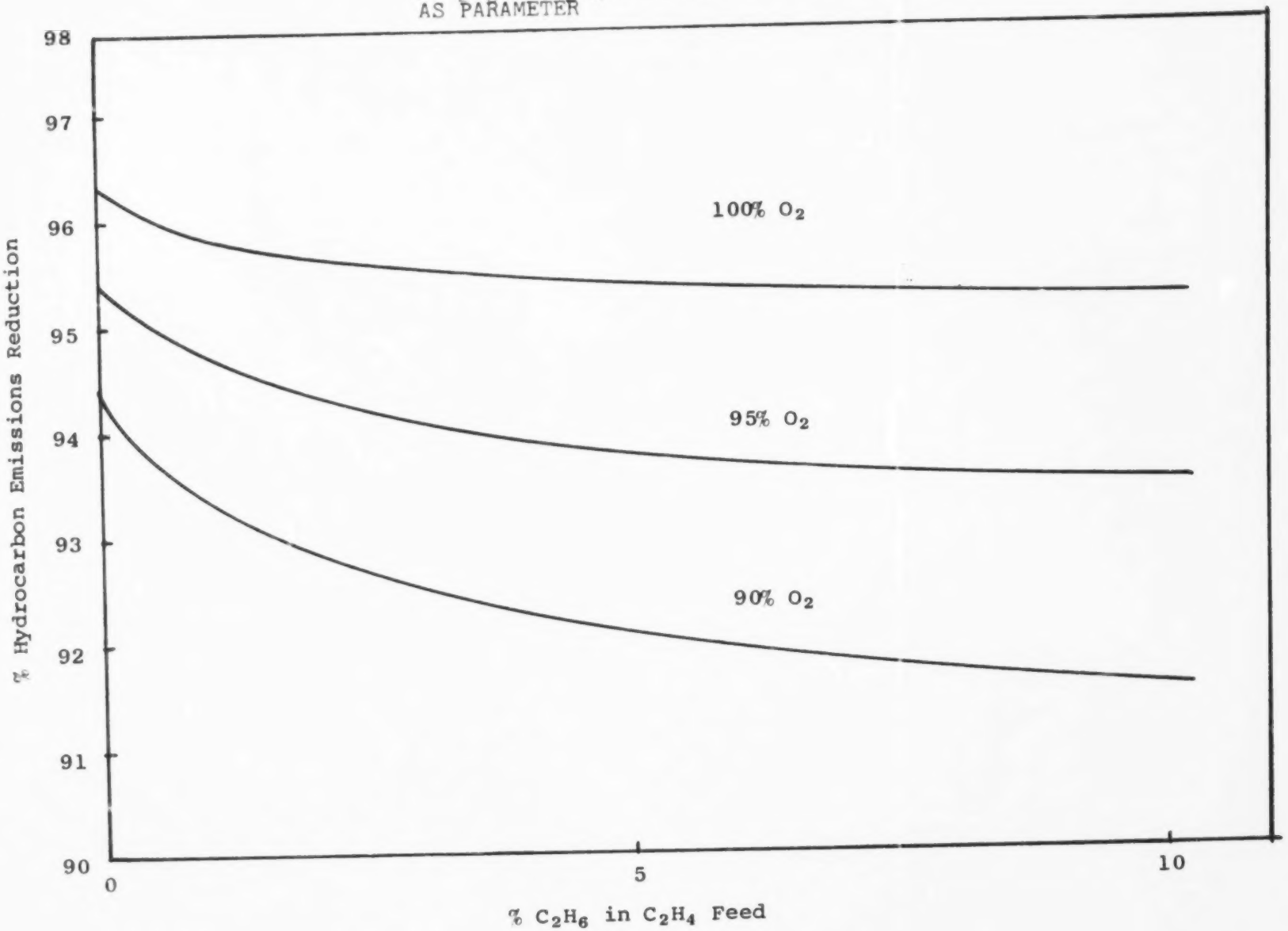


Figure 15 shows that the effect of C_2H_6 is very much less and would probably not create any difficulty since even for oxygen purities as low as 90%, all % HC emissions reduction remain above 90% for C_2H_6 from 0-10% in the feed.

With these results available and the computer simulation program capable of handling scale-up of our system, an economic analysis was performed.

ECONOMIC STUDY

The economic study had for its basis the following:

- 7% excess C_2H_4 to the reactor
- 50% excess O_2 to the reactor
- 98% pure C_2H_4 (2% CH_4)*
- 95% pure O_2 (5% N_2)
- 700 MM lbs/year EDC capacity

The study involved an Incremental Capital Cost Comparison and an Incremental Manufacturing Cost Comparison using the conventional process with air feed as the basis system. The costs necessary to convert to a recycle process with O_2 feed are outlined in Table 11 and 12. The result is that the recycle process becomes competitive with only a nominal increase in the cost of EDC/lb. Figure 16 shows how the incremental manufacturing cost in ¢/lb EDC varies with oxygen cost/NT and ethylene cost/lb. As ethylene becomes more expensive, the recycle process becomes more attractive due to its inherent higher efficiencies.

Thus, the original objective of this project has been met, viz., the development and demonstration of a recycle process for ethylene oxyhydrochlorination which will reduce by at least 90% the HC + EDC emissions over existing processes. Also, economic competitiveness for the recycle process compared to the conventional process appears fairly well demonstrated.

* Note: 2% CH_4 in C_2H_4 will mean that 90% reduction in hydrocarbons cannot be achieved, a priori. This is the economically more stringent case which (in the following economic analysis) demands that natural gas (CH_4) be added to the vent to make it combustible and then burning the vent gas in a plume burner.

TABLE 11

INCREMENTAL CAPITAL COST COMPARISON
OXYHYDROCHLORINATION SYSTEMS FOR PLANT
TO PRODUCE 700 MM LB/YR EDC

Case	1	2
Description	Conventional Process Air Feed	Recycle Process O_2 Feed
Capital Costs - M$*		
Air compressors & aux.	$ 650	$ -
Recycle compressors & aux.	-	250
EDC absorption & stripping	375	50
Vent plume	-	50
Major Equipment	$ 1,025	$ 350
Erection	115	40
Process piping	410	140
Foundations & Supports	175	60
Power wiring	100	35
Instrumentation	110	90
Paint & Insulation	50	20
Direct cost	$ 1,985	$ 735
Engineering, contingency & overheads	1,150	425
Total Cost*	$ 3,135	$ 1,160
Escalated to 1977	$ 3,450	$ 1,280

* These costs cover only those items which are not the same in the two alternate systems.

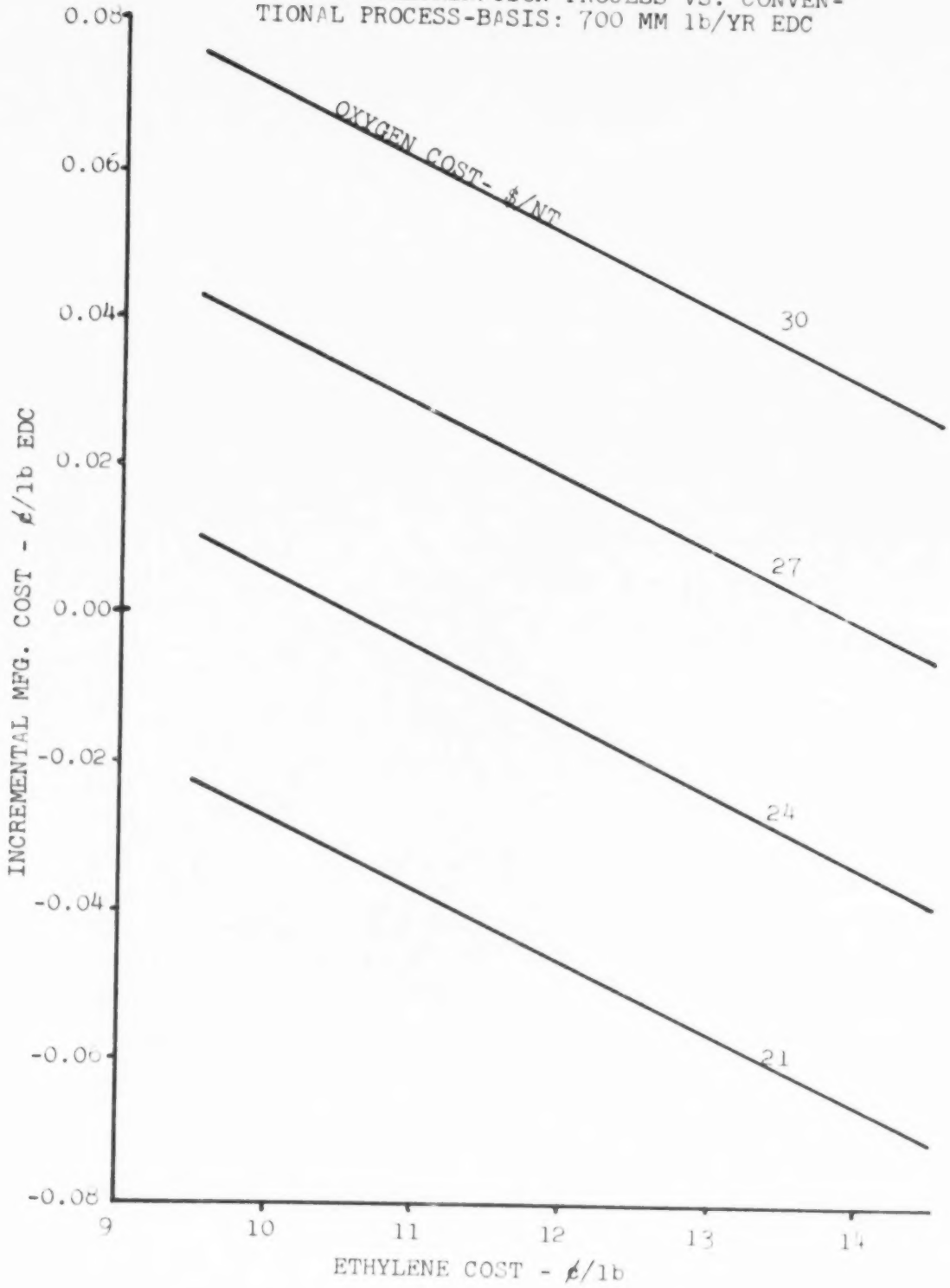
TABLE 12

INCREMENTAL MANUFACTURING COST COMPARISON
OXYHYDROCHLORINATION SYSTEMS FOR PLANT
TO PRODUCE 700 MM LB/YR EDC

Case	1	2
Description	Conventional Process Air Feed	Recycle Process O_2 Feed
Fixed Capital - M$	3,300	1,280
Manufacturing Costs - M$/Yr*		
Raw Materials & Utilities		
Oxy feed C_2H_4 at $200/NT	$ 21,997	$ 21,319
Oxy feed O_2 at $24/NT	-	1,821
Nat. gas to plume at $1.25/MCF	-	50
Electric power at $15/MKWH	254	48
Steam for stripping at $3.75/NT	22	2
Manufacturing Expense		
Maintenance & supplies at 7% of F.C.	242	90
Depreciation - 10% of F.C.	345	128
Taxes & insurance	35	13
Total cost	$ 22,895	$ 23,471
25% ROI	863	320
Total Cost*	$ 23,758	$ 23,791
Incremental cost difference		93
Unit cost ¢/lb EDC		0.0047

* These costs cover only those which are not the same for the two alternate systems.

FIGURE 16:
EFFECT OF OXYGEN AND ETHYLENE COSTS ON INCREMENTAL MFG. COST FOR RECYCLE OXYHYDROCHLORINATION PROCESS VS. CONVENTIONAL PROCESS-BASIS: 700 MM lb/YR EDC



SECTION IX

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2. Ash, S. H. and Felegy, E. W. Analysis of Complex Gas Mixtures. Bureau of Mines Bulletin. Washington, D.C. #471. 1948.

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5. Houdry report. Indepth Study of VCM Production. Contract No. 68-02-0255 for EPA by Houdry Division, Air Products and Chemicals, Inc., P.O. Box 427, Marcus Hook, PA 19061. Revised, 20 June 1975.

SECTION X

LIST OF INVENTIONS

Disclosed in U. S. Application Serial Number 587,781, filed on June 17, 1975 by W. S. Amato, B. Bandyopadhyay, B. E. Kurtz, and R. H. Fitch for Cyclic Ethylene Oxyhydrochlorination Process with Reduced Hydrocarbon Emissions.

SECTION XI

GLOSSARY

$$\text{Conversion} = \frac{\text{Quantity of Reactant Into Process} - \text{Quantity of Reactant Out of Process}}{\text{Quantity of Reactant Into Process}}$$

$$\text{Yield} = \frac{\text{Amount of Reactant Converted to Desired Product}}{\text{Amount of Reactant Converted}}$$

$$\text{Efficiency} = \text{Conversion} \times \text{Yield} = \frac{\text{Amount of Reactant Converted to Desired Product}}{\text{Amount of Reactant Fed to Process}}$$

HC - Hydrocarbons

OHC - Oxyhydrochlorination

EDC - Ethylene dichloride

Ortho - Orthodichlorobenzene (Dowtherm E)

SECTION XII

APPENDIX

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Appendix

Table 1: Once-Through Operating and Calculated Data

Run #,	Period	Date	Reactor Temperature & Pressure T °C	P psig	Superficial Velocity M/S	Ft/Sec	% xs C_2H_4	% xs Air(O_2)	HCl Flow gms/min	C_2H_4 Flow gms/min	Air Flow gms/min	CO Flow gms/min	CO_2 Flow gms/min	CH_4 Flow gms/min	C_2H_6 Flow gms/min	Cl_2 Flow gms/min	Crude Product gms/period
1,	1	9/5/74	238	39	0.448	1.47	20.0	73.5	75.0	34.6	123						2757[a]
	2	"	234	39	0.444	1.46	20.0	73.5	75.0	34.6	123						2834[a]
	3	"	228	38	0.447	1.47	20.0	73.5	75.0	34.6	123						2840[a]
2,	1	9/11/74	240	49	0.368	1.21	16.1	61.3	76.7	34.2	117						5872
	2	"	240	49	0.368	1.21	16.1	61.3	76.7	34.2							5877
	3	"	240	49	0.368	1.21	16.1	61.3	76.7	34.2							5828
3,	1	9/13/74	241	48	0.377	1.24	10.1	60.3	77.2	32.7							5966
	2	"	241	48	0.377	1.24	10.1	60.3		32.7							5764
	3	"	231	48	0.370	1.21	10.1	60.3		32.7							5844
	4	"	230	48	0.369	1.21	10.1	60.3		32.7							5912
4,	1	9/16/74	241	47	0.380	1.25	5.1	60.3		31.2							6062
	2	"	240	47.5	0.376	1.23	5.1	60.3									6135
	3	"	230	48	0.366	1.20											6033
	4	"	230	47.5	0.369	1.21											5969
5,	1	9/17/74	241	47	0.380	1.25											6094
	2	"	241	47.5	0.377	1.24											5983
	3	"	230	48	0.366	1.20											6006
	4	"	231	48	0.367	1.20											6031
6,	1	9/19/74	242	48	0.380	1.25						2.0					5991
	2	"	240	48	0.379	1.24						2.0					6.04
	3	"	231	48	0.372	1.22						2.0					5925
	4	"	231	48	0.372	1.22						2.0					5744
7,	1	9/23/74	242	48	0.382	1.25							5.0				6171
	2	"	241	48	0.381	1.25							5.0				6094
	3	"	230	49	0.368	1.21							5.0				5809
	4	"	230	48	0.373	1.22							5.0				5897
8,	1	9/26/74	241	47	0.396	1.30						8.0					6033
	2	"	243	48	0.392	1.28						8.0					5945
	3	"	230	48	0.382	1.25						8.0					5988
	4	"	231	48	0.383	1.26						8.0					5781
9,	1	10/11/74	240	48	0.375	1.23											6007
	2	"	239	48	0.374	1.23											6022
	3	"	230	48	0.368	1.21											5931
	4	"	230	48	0.368	1.21											5911
10,	1	10/16/74	240	48	0.388	1.27							11.0				5978
	2	"	240	48	0.388	1.27							11.0				6047
	3	"	230	48.5	0.377	1.24							11.0				5972
	4	"	230	48	0.380	1.25							11.0				5922
11,	1	10/18/74	232	48	0.538	1.77							150				2900[a]
	2	"	234	48	0.540	1.77							150				2769[a]
12,	1	10/18/74	238	48	0.374	1.23											5845
	2	"	232	48	0.369	1.21											6207
13,	1	10/21/74	240	48	0.375	1.23											5983
	2	"	240	48	0.375	1.23											6073
	3	"	230	48	0.368	1.21											6022
	4	"	230	48	0.368	1.21											6010

a - 30 Minute period (all other periods - 60 minutes)

Appendix

Table 1: Once-Through Operating and Calculated Data
(Continued)

Run #, Period		Date	Reactor Temperature & Pressure		Superficial Velocity		% xs C_2H_4	% xs Air(O_2)	HCl Flow gms/min	C_2H_4 Flow gms/min	Air Flow gms/min	CO Flow gms/min	CO_2 Flow gms/min	CH_4 Flow gms/min	C_2H_6 Flow gms/min	Cl_2 Flow gms/min	Crude Product gms/period
			T °C	P psig	N/S	Ft/Sec											
14,	1	10/24/74	240	48	0.375	1.23	7.6	87.7	72.5	30.0	29.8(O_2)		151.5				5712
	2	"	231	48	0.378	1.24	7.6	87.7	72.5	30.0	29.8(O_2)		151.5				5588
	3	"	235	48	0.379	1.24	7.6	87.7	72.5	30.0	29.8(O_2)		151.5				5600
	4	"	236	48	0.379	1.24	7.6	87.7	72.5	30.0	29.8(O_2)		151.5				5606
15,	1	10/29/74	237	48	0.375	1.23	5.1	60.3	77.2	31.2	117	1.25					6025
	2	"	237	48	0.375	1.23						1.25					6073
	3	"	230	48	0.370	1.21						1.25					5902
	4	"	228	49	0.363	1.19						1.25					5927
16,	1	10/31/74	240	48	0.381	1.26						5.04					5927
	2	"	241	48	0.384	1.26						5.04					5964
	3	"	231	48	0.390	1.28						12.0					5766
	4	"	239	48	0.396	1.30						12.0					5791
	5	"	240	48	0.397	1.30						12.0					5803
17,	1	11/4/74	240	48	0.375	1.23											5875
	2	"	212	48	0.376	1.24											5694
	3	"	230	48	0.368	1.21											5975
	4	"	230	48	0.368	1.21											5975
18,	1	11/27/74	250	48	0.386	1.27		73.0	72.0	30.2	118			2.35	2.21		5644
	2	"	240	48	0.379	1.24								2.35	2.21		5463
	3	"	237	48	0.376	1.23											5350
	4	"	230	48	0.371	1.22											5567
	5	"	238	48	0.374	1.23											5698
22,	1	12/13/74	241	48	0.381	1.25	12.9	72.0	74.4	32.3	121					7.27	5944
	2	"	238	48	0.379	1.24	12.9			32.3						7.27	5863
23,	1	12/16/74	240	48	0.378	1.24	8.0			30.9						3.66	6025
	2	"	241	48	0.378	1.24										3.66	6067
	3	"	230	48	0.370	1.22										3.66	5995
	4	"	230	48	0.370	1.22										3.66	5993
24,	1	12/18/74	240	48	0.378	1.24											6175
	2	"	237	48	0.375	1.23											6107
	3	"	232	48	0.372	1.22											6067
	4	"	233	48	0.373	1.22											5967
25,	1	12/23/74	240	48	0.378	1.24										0.0	5725
	2	"	240	48	0.378	1.24										3.66	5888
	3	"	240	48	0.378	1.24										3.66	5875
26,	1	12/30/74	240	48	0.378	1.24										0.0	5712
	2	"	241	48	0.378	1.24										3.66	5919
	3	"	240	48	0.378	1.24										3.66	5844

Appendix

Table 1: Once-Through Operating and Calculated Data
(Continued)

Run #,	Period	Aqueous Product gms/period	Quench Bottoms gms/period	Quench Water gms/minute	N_2 Purge Rate gms/minute	HCl in Decanter H_2O gms/period	HCl in Quench H_2O gms/period	Vent Gas Rate gm-moles/minute	% O_2	% N_2	% CO	% CO_2	% C_2H_6	% CH_4
1,	1	640	1021	44.5	4.27	0.047	0.186	4.02	4.60	87.84	1.30	3.40	2.70	
	2	560	1430	49.5	4.27	0.041	0.156	3.98	4.39	88.65	1.00	2.60	3.19	
	3	580	1300	49.5	4.27	0.021	0.142	4.03	6.08	87.56	1.00	1.70	3.49	
2,	1	1240	1663	30.0	2.64	0.090	0.420	3.72	5.69	88.85	1.10	2.99	1.50	
	2	1250	1612	30.0	2.64	0.070	0.440	3.73	2.90	88.55	1.90	3.99	2.50	
	3	1220	1774	30.0	2.64	0.060	1.03	3.73	3.49	88.65	1.60	3.89	2.20	
3,	1	1200	1820	30.0	3.42	0.060	0.620	3.76	5.29	88.66	1.30	3.59	1.00	
	2	1220	1523		3.42	0.050	0.610	3.69	2.20	90.25	1.40	4.49	1.50	
	3	1200	1272		3.42	0.060	0.500	3.72	9.38	86.65	0.60	1.90	1.30	
	4	1140	1490		3.42	0.070	0.650	3.84	5.99	88.65	0.60	2.60	2.00	
4,	1	1150	1824		3.43	0.080	1.05	3.69	5.49	90.36	1.10	2.49	0.40	
	2	1180	1543		3.42	0.090	1.68	3.71	6.19	89.85	1.20	2.10	0.50	
	3	1300	2044		3.42	0.090	5.43	3.75	8.49	88.81	0.40	0.70	1.40	
	4	1110	1358		3.42	0.120	10.8	3.79	9.18	87.95	0.70	0.60	1.40	
5,	1	1220	1205		3.43	0.067	1.27	3.70	5.20	90.14	1.10	2.90	0.50	
	2	1150	1870		3.43	0.063	1.57	3.70	5.19	90.15	1.10	2.70	0.70	
	3	1080	1764		3.43	0.090	1.73	3.77	7.69	88.81	0.60	1.30	1.30	
	4	1010	2340		3.43	0.076	1.96	3.75	7.79	88.84	0.60	1.30	1.30	
6,	1	1700	1760		4.29	0.120	2.82	3.69	4.59	91.05	1.10	2.60	0.50	
	2	1220	1762			0.090	2.89	3.75	6.60	89.54	1.10	2.20	0.40	
	3	1190	1800			0.040	2.63	3.81	7.69	88.15	0.90	1.60	1.50	
	4	1100	1720			0.080	2.70	3.82	8.49	88.05	0.70	1.30	1.30	
7,	1	1180	1466			0.120	7.66	3.84	7.49	87.45	0.80	3.89	0.20	
	2	1140	1533			0.100	5.19	3.82	5.79	88.05	0.80	4.69	0.50	
	3	1100	1703			0.080	3.10	3.91	8.69	85.35	0.60	3.89	1.50	
	4	1040	1980			0.070	3.25	3.99	9.88	84.16	0.30	2.99	2.50	
8,	1	1260	1576			0.110	1.95	3.96	4.29	84.96	5.19	4.29	1.10	
	2	1200	1874			0.110	1.84	3.95	3.80	85.11	5.10	5.00	0.50	
	3	1260	1968			0.110	2.43	4.08	6.10	82.44	6.70	2.40	2.20	
	4	1160	1898			0.100	2.89	3.86	6.89	87.15	3.79	1.00	1.00	
9,	1	1140	1864			0.083	5.56	3.80	9.58	88.35	0.50	1.00	0.40	
	2	1180	1630			0.086	13.29	3.87	11.08	86.75	0.50	0.90	0.60	
	3	1100	2240	36.0	4.26	0.060	2.70	3.79	6.99	88.75	0.60	1.60	1.90	
	4	1100	1720	30.0	4.26	0.060	2.70	3.77	6.59	89.05	0.70	1.50	2.00	
10,	1	1200	1672		4.26	0.087	3.23	4.02	5.09	83.47	0.90	9.18	1.20	
	2	1160	2220		4.26	0.085	4.13	4.02	6.49	83.56	0.70	8.09	1.00	
	3	1140	1398		4.29	0.125	14.19	4.07	8.18	82.58	0.40	6.78	1.89	
	4	1140	1654		4.26	0.125	39.65	4.12	10.39	81.54	0.10	5.80	2.00	
11,	1	920	1034			0.121	6.72	6.94	4.89	48.42	0.20	45.92	0.40	
	2	740	1240			0.081	3.26	6.93	4.79	48.52	0.20	46.02	0.30	
12,	1	1110	1934			0.081	5.21	3.80	9.27	88.46	0.40	0.80	0.90	
	2	1110	1754			0.160	22.02	3.79	8.38	88.66	0.40	0.90	1.50	
13,	1	1220	1824			0.089	1.79	3.74	5.20	89.94	0.90	2.20	1.60	
	2	1220	1473			0.089	1.66	3.77	5.90	89.04	1.00	2.50	1.40	
	3	1120	1874			0.090	3.88	3.81	8.49	88.15	0.40	0.90	1.90	
	4	1110	1884			0.081	4.80	3.82	8.59	87.95	0.40	0.60	2.30	

Appendix

Table 1: Once-Through Operating and Calculated Data
(Continued)

Run #, Period	Aqueous Products gms/period	Quench Bottoms gms/period	Quench Water gms/minute	N_2 Purge Rate gms/minute	HCl in Decanter H_2O gms/period		HCl in Quench H_2O gms/period		Vent Gas Rate gm-moles /minute	% O_2	% N_2	% CO	% CO_2	% C_2H_4	% CH_4
14, 1	1260	1500	30.0	4.29	0.322		2.19		2.23	6.29	6.89	0.80	81.96	0.90	
2	1240	1222			0.270		2.09		0.677	9.38	22.66	0.50	66.49	0.80	
3	1240	1600			0.270		1.93		1.31	5.70	11.69	0.80	81.04	0.60	
4	1240	1600			0.317		1.81		2.64	5.30	5.80	0.80	87.24	0.70	
15, 1	1240	1533		4.28	0.090		2.79		3.81	5.52	88.33	2.23	2.54	1.22	
2	1240	1242			0.090		4.16		3.82	6.54	88.02	2.11	2.02	1.15	
3	1120	1625			0.080		5.14		3.91	8.41	85.96	1.84	0.82	2.81	
4	1000	1884			0.080		5.14		3.93	9.42	85.52	1.77	0.74	2.38	
16, 1	1240	1603			0.090		4.14		3.87	4.79	86.81	4.29	2.93	1.01	
2	1220	1643		4.26	0.111		4.07		3.87	4.81	86.85	4.11	2.91	1.15	
3	1220	1824			0.089		2.99		4.27	7.21	78.66	8.84	3.16	1.96	
4	1220	1764			0.133		3.14		4.14	3.43	81.18	8.80	5.13	1.29	
5	1220	1794			0.089		2.94		4.26	7.82	78.92	7.98	3.53	1.59	
17, 1	1200	1802			0.090		2.04		3.74	4.59	89.85	1.19	2.68	1.49	
2	1210	1902			0.110		2.49		3.51	1.80	90.11	0.90	2.20	1.50	
3	1100	1784			0.120		4.09		3.85	9.58	87.35	0.50	0.90	1.50	
4	1130	1854			0.120		3.78		3.82	7.59	88.05	0.60	1.20	2.40	
18, 1	1180	1780			0.086		2.66		3.97	5.59	85.16	0.90	2.80	1.76	3.99
2	1240	980			0.090		2.14		4.11	10.68	82.26	0.60	1.70	1.50	2.99
3	1250	1563			0.091		2.16		4.13	8.59	81.84	0.70	2.20	1.90	4.30
4	1120	1900			0.082		2.84		4.16	12.58	81.36	0.40	0.70	1.20	3.29
5	1100	1790			0.120		2.55		4.02	7.10	84.14	0.10	1.70	2.30	4.00
22, 1	1320	2016			2.74	0.075[b]	20.79	0.035[c]	3.87	4.68	89.73	1.12	3.31	0.88	
2	1330	1994			2.81	0.075	23.25	0.020	4.01	8.34	86.62	1.04	3.23	0.43	
23, 1	1210	1508		4.29	1.37	0.009	13.18	0.016	3.87	5.81	89.73	0.98	2.50	0.68	
2	1230	1518		4.28	1.48	0.009	13.16	0.016	3.86	5.48	89.99	0.91	2.46	0.93	
3	1130	1735			2.10	0.012	12.33	0.047	3.92	8.34	88.48	0.55	1.38	1.03	
4	1130	1767			2.14	0.012	13.03	0.050	3.95	9.03	87.80	0.52	1.05	1.36	
24, 1	1180	1824		4.26	0.172	0.004	8.76	0.058	3.90	8.46	88.91	0.58	1.12	0.74	
2	1040	1673		4.26	0.152	0.004	11.26	0.059	3.92	9.23	88.5	0.44	0.66	1.00	
3	1140	1827		4.29	0.332	0.002	47.44	0.294	3.99	10.41	86.96	0.26	0.31	1.89	
4	1100	1973		4.29	0.201	0.002	57.45	0.220	3.97	9.52	87.49	0.28	0.30	2.24	
25, 1	1200	1902		4.26	0.088		1.99		3.89	4.92	89.30	1.02	3.45	1.14	
2	1160	1902			0.127	0.002	5.75	0.027	3.91	7.24	88.81	0.78	2.21	0.80	
3	1140	1844			0.125	0.002	5.90	0.026	3.88	5.82	89.51	0.94	2.77	0.80	
26, 1	1320	1222			0.14		2.45		3.89	6.31	89.13	0.81	2.84	0.75	
2	1290	1539			0.04	0.046	14.62	0.184	3.89	7.12	89.23	0.84	2.16	0.19	
3	1360	1271			1.09	0.116	17.09	0.138	3.91	7.68	88.71	0.71	2.13	0.29	

b - Refers to gms Cl_2/period in decanter water.

c - Refers to gms Cl_2/period in quench water.

Appendix

Table 1: Once-Through Operating and Calculated Data
(Continued)

Run #,	Period	% C_2H_6	% EDC	% Cl_2	C_2H_4 Conversion	C_2H_4 Yield	C_2H_4 Efficiency	HCl Conversion	HCl Yield	HCl Efficiency	O_2 Conversion	O_2 Yield	O_2 Efficiency	Crude EDC Purity Wt. %	Total HC + EDC Emissions Kg/Kg HCl
1,	1		0.17		91.1	82.7	75.3	100.0	90.4	90.4	79.3	65.7	52.1	98.87	0.0496
	2				89.6	86.6	77.6	100.0	93.4	93.0	80.4	66.7	53.6	98.96	0.0564
	3				88.5	88.0	77.9		93.4	93.4	72.5	74.3	53.9	99.17	0.0616
2,	1				96.2	83.6	80.5		93.5	93.4	75.1	77.2	57.9	98.33	0.0245
	2				92.3	87.1	80.4		93.3	93.3	87.3	66.3	57.8	98.36	0.0423
	3				93.2	85.7	79.8		92.7	92.7	84.7	67.9	57.5	98.25	0.0382
3,	1				96.8	88.6	85.7		94.4	94.4	76.6	76.9	58.9	98.40	0.0218
	2				95.2	86.9	82.7		91.1	91.1	90.4	62.8	56.8	98.29	0.0282
	3				95.7	88.2	84.4		92.9	92.9	57.5	100.9	58.0	98.95	0.0266
	4				93.5	91.3	85.[illegible]		94.1	94.1	73.5	79.9	58.7	99.00	0.0355
4,	1				98.6	92.6	91.3		96.0	96.0	76.2	78.6	59.9	98.50	0.0134
	2				98.3	94.0	92.4		97.1	97.1	72.9	83.0	60.6	98.50	0.0148
	3				95.3	96.6	92.0	99.9	96.8	96.6	62.4	96.6	60.3	99.28	0.0273
	4				95.2	95.2	90.6	99.8	95.5	95.3	59.0	100.8	59.4	99.34	0.0275
5,	1				98.3	93.3	91.7	100.0	96.4	96.3	77.4	77.7	60.1	98.42	0.0148
	2				97.6	92.1	89.9	100.0	94.5	94.5	77.4	76.1	58.9	98.18	0.0175
	3				93.5	97.3	91.0	100.0	95.7	95.7	65.8	90.7	59.7	99.09	0.0343
	4				95.6	95.7	91.5	100.0	96.2	96.1	65.5	91.5	60.0	99.08	0.0259
6,	1				98.3	91.7	90.3	99.9	94.8	94.8	80.0	73.9	59.1	98.34	0.0148
	2				98.6	93.3	92.0	99.9	96.8	96.7	70.8	85.2	60.3	98.55	0.0136
	3				94.8	94.7	89.8	99.9	94.5	94.4	65.4	90.0	58.9	99.09	0.0291
	4				95.5	91.2	87.1	99.9	91.6	91.5	61.8	92.4	57.2	99.09	0.0264
7,	1				99.2	93.6	92.9	99.8	97.7	97.6	66.1	92.2	60.9	98.40	0.0112
	2				98.2	93.5	91.8	99.9	96.6	96.5	73.9	81.4	60.2	98.52	0.0153
	3				94.6	93.1	88.1	99.9	92.6	92.6	50.7	96.8	57.8	99.09	0.0301
	4				91.0	100.1	91.0	99.9	95.7	95.7	53.4	111.7	59.7	99.19	0.0450
8,	1				96.0	94.8	91.1	100.0	95.7	95.7	80.0	74.6	59.7	98.64	0.0245
	2				98.1	91.4	89.7	100.0	94.3	94.3	82.3	71.4	58.8	98.57	0.0158
	3				91.9	99.0	91.0	99.9	95.7	95.6	70.7	84.4	59.7	99.27	0.0115
	4				96.5	91.1	87.9	99.9	92.4	92.4	68.7	83.9	57.6	99.34	0.0224
9,	1				98.6	92.1	90.8	99.3	95.6	95.5	57.0	104.5	59.6	98.85	0.0138
	2				97.9	96.2	94.2	99.7	99.3	99.0	49.4	125.1	61.7	98.97	0.0169
	3				93.5	96.3	90.0	99.9	94.7	94.6	68.8	85.8	59.0	99.15	0.0344
	4				93.2	94.7	88.2	99.9	92.8	92.7	70.7	81.8	57.8	99.22	0.0357
10,	1				95.6	94.5	90.3	99.9	95.0	94.9	75.9	78.1	59.1	98.72	0.0264
	2				96.3	95.1	91.5	99.9	96.3	96.2	69.2	86.7	60.0	98.86	0.0231
	3				93.0	97.5	90.6	99.7	95.5	95.2	60.7	97.8	58.4	99.20	0.0269
	4				92.5	97.1	89.8	99.1	95.2	94.4	49.5	119.0	58.9	99.09	0.0290
11,	1				97.1	91.0	88.4	99.7	93.2	92.9	60.0	96.6	58.0	98.91	0.0232
	2				97.5	86.5	84.3	99.9	88.8	88.6	60.9	90.9	55.3	98.75	0.0227
12,	1				96.9	91.3	88.4	99.9	93.0	92.9	58.5	99.2	58.0	98.84	0.0207
	2				94.9	99.0	93.9	99.5	99.2	98.7	62.6	98.4	61.6	98.97	0.0290
13,	1				94.6	95.1	90.0	100.0	94.6	94.6	77.1	76.5	59.0	98.28	0.0297
	2				95.2	95.8	91.2	100.0	95.9	95.9	73.8	81.1	59.8	98.23	0.0274
	3				93.5	97.5	91.1	99.9	95.9	95.8	61.9	96.6	59.8	98.93	0.0347
	4				92.1	98.8	91.0	99.9	95.7	95.6	61.3	97.3	59.7	98.97	0.0403

Appendix

Table 1: Once-Through Operating and Calculated Data
(Continued)

Run #,	Period	% C_2H_4	% EDC	% Cl_2	C_2H_4 Conversion	C_2H_4 Yield	C_2H_4 Efficiency	HCl Conversion	HCl Yield	HCl Efficiency	O_2 Conversion	O_2 Yield	O_2 Efficiency	Crude EDC Purity Wt. %	Total HC + EDC Emissions kg/kg HCl
14,	1		0.17		97.4	91.6	89.2	99.9	96.0	96.0	85.0	60.2	51.1	98.40	0.0120
	2				98.6	88.3	87.0	99.9	93.7	93.6	93.2	53.5	49.9	98.43	0.00367
	3				98.3	88.6	87.0	99.9	93.7	93.6	92.0	54.2	49.9	98.06	0.00609
	4				96.9	90.1	87.3	100.0	94.0	93.9	85.0	58.9	50.0	98.06	0.0133
15,	1				95.8	95.0	91.0	99.9	95.7	95.6	75.2	79.3	59.7	98.74	0.0252
	2				96.0	95.3	91.5	99.9	96.3	96.2	70.6	85.1	60.0	98.56	0.0243
	3				90.1	99.3	89.5	99.9	94.2	94.1	61.2	95.8	58.7	99.13	0.0485
	4				91.6	98.2	89.9	99.9	94.6	94.5	56.3	104.7	59.0	99.15	0.0426
16,	1				96.4	92.9	89.6	99.9	94.2	94.1	78.1	75.2	58.7	98.75	0.0227
	2				96.0	93.8	90.0	99.9	94.7	94.6	78.0	75.6	59.0	98.69	0.0246
	3				92.4	94.2	87.1	99.9	91.6	91.5	63.7	89.6	57.1	98.57	0.0398
	4				95.1	91.9	87.4	99.9	91.9	91.9	83.2	68.8	57.3	98.54	0.0284
	5				93.8	93.5	87.8	99.9	92.3	92.2	60.7	94.7	57.5	98.74	0.0339
17,	1				95.3	93.0	88.6	100.0	93.1	93.1	79.8	72.8	58.1	98.51	0.0272
	2				95.0	93.6	88.9	99.9	93.4	93.4	79.0	73.8	58.3	98.53	0.0284
	3				94.8	95.3	90.3	99.9	95.0	94.9	56.5	104.7	59.2	98.58	0.0294
	4				91.7	98.3	90.2	99.9	94.9	94.8	65.9	89.8	59.1	98.66	0.0416
18,	1	0.30			95.9	91.2	87.5	99.9	95.5	95.5	74.0	74.6	55.2	98.02	0.0665
	2	0.30			95.0	89.2	84.8	99.9	92.5	92.4	48.6	110.0	53.4	98.11	0.0629
	3	0.30			92.7	90.0	83.5	99.9	91.1	91.0	58.4	90.1	52.6	98.51	0.0850
	4	0.30			95.4	91.5	87.2	99.9	95.2	95.2	38.8	141.9	55.0	98.98	0.0648
	5	0.20			91.4	97.3	88.9	99.9	97.0	97.0	66.6	84.2	56.0	98.65	0.0846
22,	1			0.11	97.0	86.8	86.2	99.5 | 95.9[d]	89.2 | 89.2[e]	88.7 | 85.6[f]	79.4	71.3	56.6	98.03	0.0216
	2			0.17	98.5	86.3	84.9	99.4 | 93.1	88.1 | 88.1	87.6 | 82.1	62.0	89.9	55.7	97.90	0.0155
23,	1			0.14	97.6	93.7	91.4	99.7 | 89.8	94.7 | 94.7	94.4 | 85.1	74.4	77.1	57.4	98.23	0.0186
	2			0.07	96.7	95.1	91.9	99.7 | 94.9	95.0 | 95.0	94.7 | 90.2	75.9	76.0	57.7	98.11	0.0222
	3			0.06	96.3	95.0	91.5	99.7 | 95.7	94.5 | 94.5	95.2 | 90.4	62.7	91.5	57.4	98.76	0.0211
	4			0.07	95.1	96.2	91.5	99.7 | 94.8	94.6 | 94.6	94.3 | 89.7	59.3	96.9	57.5	98.82	0.0292
24,	1			0.004	97.4	96.5	94.0	99.8 | 99.7	96.8 | 96.8	96.6 | 96.5	62.4	94.6	59.0	98.53	0.0197
	2			0.0	96.4	96.6	93.2	99.7 | 100.0	96.0 | 96.0	95.8 | 96.0	58.7	99.6	58.5	98.79	0.0237
	3			0.0	93.1	99.5	92.6	98.9 | 99.9	96.2 | 96.2	95.2 | 96.1	52.6	110.6	58.2	98.82	0.0285
	4			0.0	91.9	99.0	91.0	98.7 | 99.9	94.7 | 94.7	93.5 | 94.6	56.9	100.4	57.1	98.67	0.0423
25,	1				95.9	90.7	87.0	100.0	94.0	94.0	78.2	69.9	54.6	98.30	0.0255
	2			0.0	97.1	92.2	89.5	99.9 | 100.0	92.1 | 92.1	92.0 | 92.1	67.8	82.9	56.2	98.34	0.0206
	3			0.0	97.2	91.8	89.2	99.9 | 100.0	91.8 | 91.8	91.7 | 91.8	74.3	75.4	56.0	98.23	0.0205
26,	1				97.3	89.2	86.8	99.9	93.8	93.7	72.0	75.7	54.5	98.36	0.0198
	2			0.30	99.2	90.5	89.8	99.6 | 77.2	93.7 | 93.7	93.4 | 72.4	68.5	82.3	56.4	98.26	0.0116
	3			0.32	98.9	89.7	88.7	99.6 | 75.2	92.7 | 92.7	92.3 | 69.7	65.9	84.6	55.7	98.27	0.0131

d - Cl_2 Conversion, %.
e - Cl_2 Yield, %.
f - Cl_2 Efficiency, %.

Appendix

Table 2: Recycle Operating Data

Run #	Period	Ave. Mol. Wt. Vent	T Recycle/Vent °C	Recycle Pressure psig	Uncorrected Recycle Rate g/min	Vent Pressure psig	Uncorrected Vent Rate g/min	Sample Temp. °C	Sample Pressure psig	Uncorrected Sample Vent Rate, g/min
(100)101C	1	33.63	26	63	103	67.5	1.0	24	5	1.5
	2	32.23	26.5	63	106	68.0	1.0	24	5	1.5
101D	1	35.40	30.5	65	114	68	3.5	22.5	6.0	1.65
	2	40.32	35	66	125	69	2.0	23	6.2	1.83
	3	41.92	39.5	66	132	69	5.3	23	5.8	1.81
	4	42.72	38.5	65	134	68	6.0	23	5.8	1.73
105	1	40.62	34.0	65	112	67	6.7	24.5	5.0	1.55
106	1	40.01	34.0	67	128	71	3.0	25	5.0	1.65
	2	41.27	33.5	68	129	71.5	7.0	25	6.3	1.60
107	1	40.94	31.5	68	129	71	5.7	22.5	5.5	1.48
	2	40.13	31.8	68	129	71	6.2	23.0	5.5	1.47
	3	41.43	32	68	131	71	9.0	23.5	5.5	1.51
	4	41.51	32	68	131	71	5.7	24	5.5	1.51
108	1	41.65	40	68	130	71	5.4	25	6.0	1.47
	2	42.23	40.5	68	131	71	7.0	25	5.5	1.58
	3	42.46	34	68	132	71	6.0	23	5.75	1.59
	4	41.94	33.5	69	132	71.5	5.4	22.5	5.75	1.59
109	1	41.61	32	69	128	72	5.2	24	5.3	1.63
	2	41.34	32	68	128	71.5	7.0	24.5	5.3	1.63
	3	41.07	32.2	68.5	127	71.5	5.8	24.3	5.5	1.63
	4	41.39	32.5	68	128	71.5	4.0	24	5.3	1.65
110	1	39.16	33.5	68.5	127	71.5	3.5	25	6.0	1.65
	2	41.08	33.6	67.5	127	70.5	3.0	23.5	6.0	1.67
	3	41.17	32.5	67.5	127	71	4.0	23.5	6.0	1.72
	4	42.63	32.5	68	128	71	1.5	23.5	6.0	1.76

Table 2: Recycle Operating Data
(Continued)

Run #	Period	Ave. Mol. Wt. Vent	T Recycle/Vent °C	Recycle Pressure psig	Uncorrected Recycle Rate g/min	Vent Pressure psig	Uncorrected Vent Rate g/min	Sample Temp. °C	Sample Pressure psig	Uncorrected Sample Vent Rate, g/min
111	1	41.34	31.5	67.5	129	71.5	8.7	23	6.5	1.65
	2	41.86	31	67.5	129	71	6.7	22.5	6.5	1.72
	3	42.14	31	67	131	71	4.0	22	5.9	1.73
112	1	40.36	30.2	65	123	72	9.0	22	5.5	1.52
	2	40.26	31	65.5	123	72	6.8	22	5.75	1.53
	3	41.01	31	65	124	72	7.5	22	5.5	1.53
113	1	39.48	34	67	134	75	3.7	24.5	5.0	1.63
	2	40.37	34	67	132	75.5	3.2	25	5.0	1.68
	3	41.07	33.7	67	133	75.5	2.5	24.4	5.2	1.73
	4	41.90	34	66.5	135	75	0.5	24	5.0	1.73
114	1	37.14	33.5	66	123	75	1.5	24.5	6.5	1.50
	2	39.27	33.5	65.5	123	75	2.2	25	6.5	1.55
	3	49.73	33	65.5	125	76.5	1.5	24	6.75	1.62
	4	39.95	33.5	64	120	76	3.5	23.3	6.75	1.60
115	1	41.10	31.5	64	122	79.5	2.6	21	6.2	1.68
116	1	39.83	32.5	66	132	77.5	2.5	24	6.3	1.71
	2	40.81	32.7	66	133	77.5	2.5	23.7	6.6	1.77
	3	41.70	32.5	66.5	136	73	2.5	23.5	6.8	1.87
	4	41.94	32.5	65.5	135	75.5	1.5	23.5	6.8	1.92
117	1	28.55	26.8	-	-	13	-	27	6.2	1.22
	2	28.62	27.2	-	-	13	-	25	6.3	1.22
	3	28.53	29	-	-	13	-	26	6.2	1.22
	4	28.51	27	-	-	13	-	24.5	6.2	1.24
118	1	40.85	33	63	124	71	2.0	23	6.0	1.55

Appendix

Table 2: Recycle Operating Data
(Continued)

Run #	Period	HCl Feed g/min	HCl Feed Gmoles/min	C_2H_4 Feed g/min	C_2H_4 Feed Gmoles/min	O_2 Feed g/min	O_2 Feed Gmoles/min	N_2/CO_2 Pressure psig	N_2/CO_2 Flow g/min
(100)101C	1	75.6	2.073	29.3	1.043	20.4	0.638	100	2.81 (N_2)
	2	75.6	2.073	29.3	1.043	20.8	0.650	100	2.81 (N_2)
(101)101D	1	75.6	2.073	30.2	1.075	21.4	0.669	100	3.76 (CO_2)
	2	75.6	2.073	30.8	1.097	23.4	0.731	100	3.76 (CO_2)
	3	75.6	2.073	30.8	1.097	23.4	0.731	100	3.76 (CO_2)
	4	75.6	2.073	30.8	1.097	23.4	0.731	100	3.76 (CO_2)
105	1	75.6	2.073	31.2	1.111	25.3	0.791	100	3.76 (CO_2)
106	1	75.6	2.073	31.2	1.111	24.3	0.759	100	3.76 (CO_2)
	2	75.6	2.073	31.2	1.111	24.3	0.759	100	3.76 (CO_2)
107	1	75.6	2.073	32.5	1.157	26.8	0.838	100	3.76 (CO_2)
	2	75.6	2.073	32.5	1.157	27.3	0.853	100	3.76 (CO_2)
	3	75.6	2.073	32.5	1.157	27.3	0.853	100	3.76 (CO_2)
	4	73.7	2.021	32.5	1.157	27.3	0.853	100	3.76 (CO_2)
108	1	75.6	2.073	31.2	1.111	24.3	0.759	100	3.76 (CO_2)
	2	75.6	2.073	31.2	1.111	25.3	0.791	100	3.76 (CO_2)
	3	75.6	2.073	31.2	1.111	25.3	0.791	100	3.76 (CO_2)
	4	75.6	2.073	31.2	1.111	25.3	0.791	100	3.76 (CO_2)
109	1	75.6	2.073	31.2	1.111	25.3	0.791	100	3.76 (CO_2)
	2	75.6	2.073	31.2	1.111	26.3	0.822	100	3.76 (CO_2)
	3	75.6	2.073	31.2	1.111	26.1	0.816	88	3.56 (CO_2)
	4	75.6	2.073	31.2	1.111	25.8	0.806	50	1.70 (CO_2)
110	1	75.6	2.073	31.8	1.132	27.3	0.853	25	0.177 (CO_2)
	2	75.6	2.073	31.8	1.132	27.3	0.853	25	0.133 (CO_2)
	3	75.6	2.073	31.8	1.132	27.3	0.853	33	0.485 (CO_2)
	4	75.6	2.073	31.8	1.132	27.3	0.853	33	0.146 (CO_2)

Appendix

Table 2: Recycle Operating Data
(Continued)

Run #	Period	HCl Feed g/min	HCl Feed Gmoles/min	C_2H_4 Feed g/min	C_2H_4 Feed Gmoles/min	O_2 Feed g/min	O_2 Feed Gmoles/min	N_2/CO_2 Pressure psig	N_2/CO_2 Flow g/min
111	1	75.6	2.073	32.3	1.150	29.2	0.913	42	0.529 (CO_2)
	2	75.6	2.073	32.3	1.150	28.3	0.884	41	0.525 (CO_2)
	3	75.6	2.073	32.3	1.150	28.3	0.884	39	0.515 (CO_2)
112	1	75.6	2.073	32.3	1.150	28.3	0.884	50	0.509 (CO_2)
	2	75.6	2.073	33.0	1.175	28.3	0.884	50	0.396 (CO_2)
	3	75.6	2.073	33.0	1.175	28.3	0.884	50	0.396 (CO_2)
113	1	75.6	2.073	30.3	1.079	22.8	0.713	50	0.565 (CO_2)
	2	75.6	2.073	30.3	1.079	22.8	0.713	50	0.565 (CO_2)
	3	75.6	2.073	30.3	1.079	22.4	0.700	50	0.565 (CO_2)
	4	75.6	2.073	30.3	1.079	22.0	0.688	50	0.565 (CO_2)
114	1	75.6	2.073	30.8	1.097	21.4	0.669	50	0.565 (CO_2)
	2	75.6	2.073	30.8	1.097	22.8	0.713	50	0.565 (CO_2)
	3	75.6	2.073	30.3	1.079	22.8	0.713	50	0.565 (CO_2)
	4	75.6	2.073	30.3	1.079	22.0	0.688	50	0.565 (CO_2)
115	1	75.6	2.073	30.8	1.097	24.0	0.750	50	0.565 (CO_2)
116	1	75.6	2.073	30.8	1.097	23.75	0.742	60	0.425 (CO_2)
	2	75.6	2.073	31.0	1.104	23.0	0.719	60	0.425 (CO_2)
	3	75.6	2.073	31.0	1.104	23.0	0.719	60	0.425 (CO_2)
	4	75.6	2.073	31.0	1.104	23.0	0.719	60	0.425 (CO_2)
117	1	75.6	2.073	30.6	1.090	121.6(Air)	4.193(Air)	63.5	4.454 (N_2)
	2	75.6	2.073	30.6	1.090	121.6(Air)	4.193(Air)	63.5	4.454 (N_2)
	3	75.6	2.073	30.6	1.090	121.6(Air)	4.193(Air)	63.5	4.454 (N_2)
	4	75.6	2.073	30.6	1.090	121.6(Air)	4.193(Air)	63.5	4.454 (N_2)
118	1	75.6	2.073	28.3	1.008	20.0	0.625	50	0.723 (CO_2)

Appendix

Table 2: Recycle Operating Data
(Continued)

Run #	Period	N_2 / CO_2 Flow Cmoles/min	Reactor P	Reactor T	Quench gms/min	Crude Product gms/period	Decanter Water gms/period	Quench Bottoms gms/period	HCl in Decanter H_2O gms/period	HCl in Quench gms/period	Period min	Date
(100)101C	1	0.10 (N_2)	46	246	32.5	6071	1060	1947	0.300	14.9	60	3/4/75
	2	0.10 (N_2)	47	244	30.0	4566	720	1560	0.140	16.06	45	"
(101)101D	1	0.0855(CO_2)	45.5	250	30	6214	1365	1857	0.443	34.76	60	3/7/75
	2	0.0855(CO_2)	46	249	30	5936	1105	1715	0.517	17.52	60	"
	3	0.0855(CO_2)	46	244	30	6413	1210	1866	0.427	16.69	60	"
	4	0.0855(CO_2)	46	242	30	6373	1235	1884	0.355	13.50	60	"
105	1	0.0855(CO_2)	46	242	30	6301	1250	1630	1.30	8.09	60	3/13/75
106	1	0.0855(CO_2)	46	241	30	6302	1229	1782	0.355	5.45	60	3/14/75
	2	0.0855(CO_2)	46	242	30	6244	1229	1663	0.311	2.72	60	"
107	1	0.0855(CO_2)	45	244	30	6484	1578	1914	0.373	2.089	60	3/18/75
	2	0.0855(CO_2)	45	244	30	6357	1282	1962	0.350	1.64	60	"
	3	0.0855(CO_2)	45	241	30	6325	1301	1884	0.332	1.85	60	"
	4	0.0855(CO_2)	45	244	30	6312	1301	1683	0.308	2.57	60	"
108	1	0.0855(CO_2)	45	244	30	6380	1220	1922	0.222	1.68	60	3/19/75
	2	0.0855(CO_2)	45.5	244	30	6365	1210	1892	0.24	2.21	60	"
	3	0.0855(CO_2)	45	241	30	6305	1200	1842	0.26	1.87	60	"
	4	0.0855(CO_2)	46	239	30	6401	1190	1962	0.30	2.00	60	"
109	1	0.0855(CO_2)	45	243	23	6272	1241	1643	0.27	2.51	60	3/20/75
	2	0.0855(CO_2)	45	241	23	6330	1281	1583	0.28	2.65	60	"
	3	0.0808(CO_2)	45	240	34.8	6270	1221	1894	0.27	2.98	60	"
	4	0.0385(CO_2)	45	241	30	6296	1221	1824	0.22	2.72	60	"
110	1	0.00402(CO_2)	45	251	30	6211	1310	1486	0.43	8.63	60	3/21/75
	2	0.00302(CO_2)	45	251	32.5	6359	1320	1729	0.48	14.43	60	"
	3	0.0110(CO_2)	45	251	30	6349	1340	1650	0.49	22.73	60	"
	4	0.00331(CO_2)	45	249	30	6655	1310	1759	0.43	13.72	60	"

Table 2: Recycle Operating Data
(Continued)

Run #	Period	N_2 / CO_2 Flow Gmoles/min	Reactor P	Reactor T	Quench gms/min	Crude Product gms/period	Decanter Water gms/period	Quench Bottoms gms/period	HCl In Decanter H_2O gms/period	HCl in Quench gms/period	Period min	Date
111	1	0.0120(CO_2)	45	254	30	6286	1282	1851	0.33	1.74	60	3/31/75
	2	0.0118(CO_2)	45	252	30	6453	1267	1645	0.23	2.44	60	"
	3	0.0117(CO_2)	45	251	30	6309	1252	1779	0.23	2.45	60	"
112	1	0.0116(CO_2)	45	252	30	6312	1509	1544	0.38	7.36	60	4/1/75
	2	0.00899(CO_2)	45	252	30	6417	1319	1648	0.29	14.98	60	"
	3	0.00899(CO_2)	45	251	30	6455	1301	1818	0.38	12.67	60	"
113	1	0.0128(CO_2)	45	231	30	6226	1124	1555	0.24	0.73	60	4/2/75
	2	0.0128(CO_2)	45	231	30	6175	1173	974	0.21	0.71	60	"
	3	0.0128(CO_2)	45	230	30	6255	1142	1242	0.25	0.68	60	"
	4	0.0128(CO_2)	45	230	30	6304	942	1804	0.21	1.38	60	"
114	1	0.0128(CO_2)	45	231	30	6303	1163	1363	0.21	2.83	60	4/3/75
	2	0.0128(CO_2)	45	231.7	30	6201	1147	1764	0.21	2.31	60	"
	3	0.0128(CO_2)	45	230	30	6242	1106	1623	0.24	1.83	60	"
	4	0.0128(CO_2)	44	231	30	6349	1165	1633	0.21	2.79	60	"
115	1	0.0128(CO_2)	45	238	30	6378	1165	1473	0.59	6.07	60	4/8/75
116	1	0.00966(CO_2)	45	232	30	6273	1101	1914	0.20	0.56	60	4/9/75
	2	0.00966(CO_2)	45	231	28.8	6306	1320	1952	0.29	0.92	60	"
	3	0.00966(CO_2)	45	230	30	6417	1150	1734	0.29	0.89	60	"
	4	0.00966(CO_2)	45	229	30	6448	1150	1633	0.25	1.07	60	"
117	1	0.159(N_2)	45	239	30	6014	1170	1873	0.13	3.40	60	4/10/75
	2	0.159(N_2)	45.5	242	30	6002	1150	2072	0.13	5.13	60	"
	3	0.159(N_2)	45	232	30	5955	1140	1673	0.12	4.90	60	"
	4	0.159(N_2)	45	230	30	6012	1150	1613	0.15	4.60	60	"
118	1	0.0164(CO_2)	44	223	30	1543	301	521	0.055	0.27	15	4/11/75

Appendix

Table 3: Calculated Recycle Data

Run #,	Period	Rx T °C	Rx P psig	% xs C_3H_8	% xs O_2	Gmoles/hr HCl	Ave. Mol. Weight Vent & Recycle	Superficial Velocity M/S	Superficial Velocity Ft/S	Recycle Rate KG/Hr	Recycle Rate KGmoles/hour	Total Vent Rate KG/Hr	Total Vent Rate KGmoles/hour
100,	1	246	46	14.6	57.2	124.38	33.91	0.337	1.106	5.043	0.1593	0.266	0.0078
	2	244	47	21.5	75.5	"	33.16	0.338	1.111	5.556	0.1675	0.266	0.0080
101,	1	250	45.5	4.9	83.0	"	35.92	0.353	1.158	6.012	0.1674	0.412	0.0115
	2	249	46	6.7	61.4	"	40.41	0.350	1.149	6.585	0.1630	0.343	0.0085
	3	244	46	7.0	60.5	"	42.08	0.348	1.141	6.903	0.1641	0.515	0.0122
	4	242	46	8.3	52.5	"	42.82	0.345	1.133	6.975	0.1629	0.546	0.0128
105,	1	242	46	9.2	68.0	"	40.67	0.333	1.093	5.873	0.1444	0.570	0.0140
106,	1	241	46	10.0	77.5	"	40.08	0.353	1.157	6.795	0.1696	0.384	0.0096
	2	242	46	10.5	60.8	"	41.43	0.351	1.151	6.896	0.1664	0.603	0.0146
107,	1	244	45	16.5	74.9	"	41.02	0.366	1.201	6.918	0.1686	0.523	0.0127
	2	244	45	20.4	86.0	"	40.21	0.370	1.214	6.915	0.1720	0.549	0.0137
	3	241	45	21.6	75.3	"	41.50	0.365	1.199	7.020	0.1692	0.704	0.0170
	4	244	45	30.8	75.3	121.25	41.57	0.364	1.196	7.020	0.1689	0.688	0.0166
108,	1	244	45	10.8	55.9	124.38	41.72	0.356	1.169	6.877	0.1648	0.503	0.0120
	2	244	45.5	11.3	60.8	"	42.33	0.354	1.161	6.924	0.1636	0.594	0.0140
	3	241	45	12.1	62.0	"	42.58	0.356	1.169	7.050	0.1656	0.545	0.0128
	4	239	46	11.3	94.6	"	42.02	0.350	1.149	6.991	0.1664	0.514	0.0122
109,	1	243	45	9.7	71.5	"	41.68	0.358	1.174	6.900	0.1655	0.506	0.0121
	2	241	45	9.7	101.5	"	41.40	0.358	1.175	6.859	0.1657	0.603	0.0146
	3	240	45	13.2	115.2	"	41.17	0.359	1.178	6.824	0.1658	0.538	0.0131
	4	241	45	11.0	113.2	"	41.49	0.357	1.171	6.853	0.1052	0.440	0.0106
110,	1	251	45	13.5	71.6	"	39.42	0.374	1.228	6.809	0.1727	0.414	0.0105
	2	251	45	11.2	70.7	"	41.24	0.367	1.202	6.767	0.1641	0.387	0.0094
	3	251	45	10.4	74.3	"	41.40	0.366	1.201	6.779	0.1638	0.446	0.0108
	4	249	45	10.7	68.4	"	42.92	0.361	1.185	6.853	0.1597	0.312	0.0073

Appendix

Table 3: Calculated Recycle Data
(Continued)

Run #,	Period	Rx T °C	Rx P psig	% xs C_2H_4	% xs O_2	Gmoles/hr HCl	Ave. Mol. Weight Vent & Recycle	Superficial Velocity		Recycle Rate		Total Vent Rate	
								M/S	Ft/S	KG/hr	KGmoles/hour	KG/hr	KGmoles/hour
111,	1	254	45	12.4	100.3	124.38	41.46	0.375	1.230	6.897	0.1664	0.701	0.0169
	2	252	45	12.2	105.3	"	41.90	0.370	1.215	6.903	0.1648	0.595	0.0142
	3	251	45	12.2	110.7	"	42.23	0.370	1.215	6.989	0.1655	0.447	0.0106
112,	1	252	45	17.5	76.5	"	40.55	0.366	1.201	6.490	0.1600	0.710	0.0175
	2	252	45	20.0	78.1	"	40.30	0.369	1.210	6.501	0.1613	0.589	0.0146
	3	251	45	18.6	78.0	"	41.04	0.366	1.201	6.534	0.1592	0.627	0.0153
113,	1	231	45	14.6	73.8	"	39.66	0.356	1.167	7.114	0.1794	0.425	0.0107
	2	231	45	13.6	71.1	"	40.69	0.350	1.147	7.008	0.1722	0.401	0.0099
	3	230	45	13.0	70.2	"	41.29	0.347	1.139	7.064	0.1711	0.366	0.0089
	4	230	45	12.1	55.0	"	42.11	0.345	1.133	7.145	0.1697	0.254	0.0060
114,	1	231	45	12.6	62.0	"	37.35	0.350	1.147	6.495	0.1739	0.299	0.0080
	2	231.7	45	12.4	63.1	"	38.80	0.346	1.136	6.475	0.1669	0.341	0.0088
	3	230	45	10.9	60.0	"	40.93	0.339	1.112	6.586	0.1609	0.306	0.0075
	4	231	44	9.2	71.4	"	40.27	0.339	1.112	6.258	0.1554	0.418	0.0104
115,	1	238	45	8.4	82.6	"	41.33	0.342	1.121	6.383	0.1544	0.375	0.0091
116,	1	232	45	14.0	77.7	"	40.14	0.354	1.162	6.982	0.1739	0.369	0.0092
	2	231	45	16.7	55.6	"	41.14	0.350	1.148	7.032	0.1709	0.374	0.0091
	3	230	45	18.8	49.2	"	41.92	0.350	1.150	7.215	0.1721	0.381	0.0091
	4	229	45	17.8	53.1	"	42.46	0.346	1.135	7.118	0.1676	0.382	0.0090
117,	1	239	45	5.3	70.1	"	28.75	0.398	1.305	0	0	6.668	0.2319
	2	245	45.5	5.3	70.1	"	28.75	0.399	1.310	0	0	6.744	0.2346
	3	232	45	5.3	70.1	"	28.66	0.392	1.287	0	0	6.761	0.2359
	4	230	45	5.3	70.1	"	28.61	0.391	1.282	0	0	6.759	0.2363
118,	1	223	44	4.6	77.9	"	40.99	0.328	1.076	6.430	0.1569	0.206	0.0050

Appendix

Table 3: Calculated Recycle Data
(Continued)

Run #, Period	Total Feeds Incl. Recycle KG/hr	Recycle Kgmoles/hour	Vol. % Recycled	Total HC + EDC Emissions kG Kg HCl	HCl Conv. %	HCl Yield %	HCl Efficiency %	C_2H_4 Conv. %	C_2H_4 Yield %	C_2H_4 Efficiency %
100, 1	12.91	0.3843	95.31	0.00341	99.7	97.3	97.0	98.7	97.4	96.2
2	13.09	0.3933	95.44	0.00431	99.5	97.9	97.4	98.4	98.2	96.7
101, 1	13.63	0.3962	93.59	0.00236	99.2	100.2	99.4	98.9	96.8	95.7
2	14.36	0.3967	95.05	0.00046	99.6	95.1	94.7	99.6	89.7	89.4
3	14.68	0.3978	93.05	0.00112	99.6	102.6	102.2	99.0	97.5	96.5
4	14.75	0.3967	92.74	0.00127	99.7	102.1	101.7	98.8	97.2	96.0
105, 1	13.79	0.3826	91.15	0.00102	99.8	100.6	100.4	99.4	94.1	93.5
106, 1	14.65	0.4059	94.65	0.00087	99.9	100.7	100.6	99.1	94.6	93.7
2	14.75	0.4028	91.96	0.00204	99.9	99.3	99.2	98.8	93.5	92.4
107, 1	15.00	0.4124	92.97	0.00178	99.9	103.8	103.7	98.9	93.9	92.8
2	15.03	0.4166	92.64	0.00292	100.0	101.8	101.8	99.1	91.9	91.0
3	15.13	0.4138	90.88	0.00435	100.0	101.2	101.1	98.3	92.0	90.4
4	15.02	0.4104	91.07	0.00858	99.9	103.4	103.3	97.7	92.2	90.1
108, 1	14.73	0.4011	93.19	0.00136	100.0	101.8	101.7	98.8	95.9	94.8
2	14.84	0.4017	92.10	0.00193	99.9	101.2	101.2	98.7	95.5	94.3
3	14.96	0.4038	92.82	0.00205	100.0	100.4	100.3	98.7	94.7	93.5
4	14.91	0.4046	93.15	0.00156	99.9	102.2	102.2	98.8	96.4	95.2
109, 1	14.81	0.4037	93.17	0.00106	99.9	99.8	99.8	98.9	94.0	93.0
2	14.83	0.4057	91.92	0.00121	99.9	100.6	100.6	98.8	94.9	93.7
3	14.84	0.4076	92.69	0.00129	99.9	100.0	100.0	98.8	91.3	90.3
4	14.80	0.4043	93.96	0.00139	99.9	100.5	100.4	98.9	94.6	93.5
110, 1	14.88	0.4159	94.27	0.00203	99.8	99.1	99.0	99.2	91.2	90.5
2	14.84	0.4073	94.58	0.00103	99.7	101.5	101.2	99.1	93.3	92.5
3	14.85	0.4069	93.83	0.00124	99.5	101.3	100.8	99.1	93.0	92.1
4	14.92	0.4129	95.64	0.00107	99.7	106.1	105.8	99.1	97.6	96.7

Table 3: Calculated Recycle Data
(Continued)

Run #, Period	Total Feeds Incl. Recycle KG/hr	Total Feeds Incl. Recycle KGmoles/hour	Vol. % Recycled	Total HC + EDC Emissions KG/Kg HCl	HCl Conv. %	HCl Yield %	HCl Efficiency %	C_2H_4 Conv. %	C_2H_4 Yield %	C_2H_4 Efficiency %
112, 1	14.65	0.4061	90.14	0.00415	99.8	100.7	100.6	98.8	91.7	90.5
2	14.70	0.4089	91.69	0.00264	99.7	102.3	102.0	98.5	91.2	89.8
3	14.73	0.4068	91.24	0.00223	99.7	103.2	102.9	99.0	91.6	90.7
113, 1	14.82	0.4110	94.36	0.00316	100.0	100.1	100.0	98.6	97.4	96.0
2	14.72	0.4038	94.59	0.00331	100.0	99.3	99.3	98.7	96.5	95.3
3	14.75	0.4019	95.08	0.00255	100.0	100.4	100.4	98.5	97.8	96.4
4	14.81	0.3998	96.57	0.00158	100.0	101.4	101.4	98.9	98.4	97.3
114, 1	14.15	0.4040	95.61	0.00181	99.9	101.2	101.2	98.8	96.7	95.5
2	14.22	0.3995	95.00	0.00199	99.9	98.8	99.7	99.2	94.8	94.1
3	14.30	0.3925	95.54	0.00181	100.0	100.4	100.4	99.3	97.0	96.3
4	13.92	0.3855	93.74	0.00256	99.9	102.3	102.3	99.3	98.8	98.1
115, 1	14.20	0.3893	94.45	0.00146	99.9	102.1	101.9	99.1	97.0	96.2
116, 1	14.78	0.4084	94.98	0.00276	100.0	100.8	100.8	98.7	96.3	95.1
2	14.80	0.4044	94.95	0.00326	100.0	101.5	101.5	98.7	96.4	95.1
3	14.98	0.4056	94.98	0.00326	100.0	103.1	103.1	98.5	98.1	96.7
4	14.88	0.4011	94.90	0.00416	100.0	103.6	103.6	98.4	98.7	97.2
117, 1	13.94	0.4524	0	0.02126	99.9	97.7	97.6	98.2	94.5	92.7
2	13.94	0.4524	0	0.01776	99.9	97.1	97.0	97.8	94.2	92.2
3	13.94	0.4524	0	0.02993	99.9	96.8	96.7	94.9	96.7	91.8
4	13.94	0.4524	0	0.02597	99.9	97.6	97.5	95.3	97.2	92.6
118, 1	13.86	0.3790	96.89	0.00125	100.0	99.8	99.8	99.8	102.8	102.5

Appendix

Table 3: Calculated Recycle Data
(Continued)

Run #,	Period	O_2 Conv. %	O_2 Yield %	O_2 Efficiency %	Vent O_2 %	Vent N_2 %	Vent CO %	Vent CO_2 %	Vent C_2H_4 %	Vent CH_4 %	Vent C_2H_6 %	Vent EDC %	EDC Purity Wt. %
100,	1	98.6	80.6	79.5	6.87	45.80	8.16	33.25	5.38	0	0.10	0.44	97.85
	2	98.0	79.9	78.3	9.48	46.68	7.08	28.73	7.68	0	0.10	0.26	97.94
101,	1	97.1	80.0	77.7	10.22	40.96	4.26	43.29	0.40	0	0.05	0.82	97.86
	2	99.2	68.2	67.6	4.09	15.68	3.89	75.84	0.30	0	0.05	0.15	97.74
	3	98.9	73.8	73.0	3.89	5.88	3.69	85.76	0.40	0	0.10	0.28	97.61
	4	99.3	73.2	72.7	2.40	1.80	3.49	91.18	0.90	0	0.05	0.19	97.78
105,	1	98.9	67.0	66.3	3.60	14.29	3.30	77.88	0.80	0	0.05	0.09	97.55
106,	1	98.8	70.1	69.2	5.89	16.88	2.50	73.52	1.00	0	0.10	0.11	97.74
	2	99.1	68.9	68.2	2.89	10.77	2.89	81.91	1.20	0	0.05	0.29	97.25
107,	1	99.3	65.2	64.7	2.70	9.79	5.49	80.11	1.75	0	0.03	0.14	97.79
	2	98.9	63.0	62.3	4.10	12.69	5.10	74.89	3.10	0	0.04	0.09	97.89
	3	99.3	62.4	61.9	2.20	4.99	5.89	83.15	3.59	0	0.03	0.15	97.74
	4	99.5	62.0	61.7	1.40	1.20	7.59	83.86	5.79	0	0.03	0.13	97.64
108,	1	99.5	70.4	70.0	2.00	7.49	4.29	84.70	1.30	0	0.10	0.12	97.52
	2	99.5	67.2	66.9	1.80	3.09	4.99	88.34	1.50	0	0.10	0.18	97.28
	3	99.5	66.6	66.3	2.00	1.70	4.59	89.66	1.80	0	0.05	0.21	97.36
	4	97.9	69.0	67.5	8.09	2.60	2.70	84.93	1.50	0	0.05	0.14	97.68
109,	1	99.0	66.6	65.9	3.79	8.49	2.70	83.93	0.90	0	0.05	0.14	97.35
	2	97.5	65.6	63.9	8.29	6.79	2.60	81.22	0.90	0	0.10	0.10	97.25
	3	97.0	66.0	64.0	11.08	6.99	2.00	78.77	0.90	0	0.10	0.17	97.57
	4	97.6	66.7	65.1	11.08	4.09	2.50	80.70	1.40	0	0.05	0.19	97.57
110,	1	99.7	60.8	60.6	1.49	17.62	9.86	69.04	1.49	0	0.05	0.45	97.47
	2	99.7	62.1	61.9	1.40	9.47	6.98	81.11	0.70	0	0.05	0.29	97.31
	3	99.6	62.0	61.7	2.09	7.67	7.97	81.42	0.40	0	0.05	0.40	97.11
	4	99.9	64.9	64.8	0.99	2.49	4.78	90.68	0.50	0	0.05	0.52	97.26

Appendix

Table 3: Calculated Recycle Data
(Continued)

Run #,	Period	O_2 Conv. %	O_2 Yield %	C_2 Efficiency %	Vent O_2 %	Vent N_2 %	Vent CO %	Vent CO_2 %	Vent C_2H_4 %	Vent CH_4 %	Vent C_2H_4 %	Vent EDC %	EDC Purity Wt. %
112,	1	99.5	59.7	59.4	1.40	6.48	12.65	76.53	2.49	0.05	0.05	0.36	97.38
	2	99.5	60.5	60.2	1.70	3.80	15.78	76.03	2.50	0.05	0.05	0.10	97.26
	3	99.5	61.1	60.8	1.70	4.40	10.99	80.74	2.00	0.05	0.05	0.08	97.53
113,	1	98.4	74.6	73.4	6.48	17.41	2.29	69.83	3.59	0	0.05	0.32	98.31
	2	98.5	73.9	72.8	6.27	12.53	1.89	75.28	3.38	0	0.10	0.55	98.43
	3	98.6	76.0	74.9	6.57	7.97	2.09	79.69	3.19	0	0.10	0.39	98.35
	4	99.4	77.5	77.0	4.28	5.18	1.69	85.50	2.89	0	0.10	0.35	98.47
114,	1	98.8	80.0	79.0	6.08	33.39	2.29	55.42	2.39	0	0.10	0.33	98.32
	2	99.0	73.9	73.1	4.98	25.22	2.19	64.78	2.39	0	0.10	0.33	98.42
	3	99.2	74.2	73.6	4.68	11.96	2.19	78.13	2.59	0	0.10	0.34	98.49
	4	98.0	79.3	77.7	7.96	15.32	1.79	72.31	1.99	0	0.10	0.54	98.51
115,	1	98.4	72.1	71.0	7.87	8.17	2.89	79.52	1.00	0.05	0.10	0.42	97.83
116,	1	98.7	71.9	70.9	6.37	16.02	2.19	71.92	2.88	0	0.10	0.53	98.31
	2	99.3	74.3	73.7	3.28	11.73	1.89	78.75	3.68	0	0.10	0.57	98.45
	3	99.6	75.2	74.9	2.09	6.53	1.69	84.79	4.38	0	0.10	0.37	98.32
	4	99.4	75.8	75.3	2.87	4.46	1.88	85.61	4.16	0	0.10	0.91	98.27
117,	1	71.1	80.7	57.4	6.58	90.05	0.80	1.79	0.50	0	0	0.28	
	2	69.9	81.6	57.0	6.79	89.34	0.90	2.20	0.60	0	0	0.18	
	3	66.2	85.9	56.8	7.59	88.84	0.60	1.40	1.40	0	0	0.19	
	4	64.3	89.1	57.3	7.99	88.88	0.50	1.20	1.30	0	0	0.14	
118,	1	98.4	84.7	83.4	11.56	5.58	2.49	77.06	2.89	0.05	0.10	0.28	98.90